HL Chemistry Notes (2016 syllabus)

"Chemists do not usually stutter. It would be very awkward if they did, seeing that they, at times, must say words like methylethylamylophenylium"

-Sir William Crookes

"The first gulp from the glass of the Natural Sciences will turn you into an atheist, but at the bottom of the glass, God is waiting for you."

-Werner Heisenberg

Contents

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①

Moles + Calculations

Avogadro

→ constant = 6.02×10^{23} atoms per mole

$$\text{Moles} = \frac{\text{mass (g)}}{\text{RFM/RAM}}$$

Relative Atomic Mass (RAM)

→ Average mass of all isotopes of an element compared to $\frac{1}{12}$ the mass of a C_{12} atom

Relative Molecular Mass (RMM)

→ mass of all atoms in a molecule compared to 1/12 the mass of C_{12} atom

Ionic Equations

E.g → $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(\overset{s}{\cancel{aq}}) + NaNO_3(aq)$

$Ag^+ NO_3^- + Na^+ Cl^- \rightarrow AgCl(s) + Na^+ + NO_3^-$

Cancel out ions that stay ions on RHS + LHS

$\therefore Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl(s)$

Empirical Formula

E.g 50g of a compound contains 22.4g of K, 9.2 of S and the remaining oxygen. Find the ~~remaining~~ empirical formula

$50 - 22.4 - 9.2 = 18.4$

K	S	O
$\frac{22.4g}{39}$	$\frac{9.2g}{32}$	$\frac{18.4g}{16}$
0.574 :	0.2875 :	1.15

↓ ÷ all by smallest number

$\therefore$ 2 : 1 : 4

Hence the formula is $\underline{K_2SO_4}$

Atom economy

$$\frac{\text{Desired Product Mass}}{\text{Total Products mass}} \times 100\%$$

Yield

$$\frac{\text{Mass of products}}{\text{max theoretical mass}} \times 100\%$$

Limiting Reagents → reagent not in excess

~~$2SO_2$ +~~ E.g In making Ti, what mass of Ti can be formed when 1kg of $TiCl_4$ reacts with 0.1kg of Mg

$$\frac{100g}{24.3} = 4.115$$

$$TiCl_4(s) + 2Mg(s) \rightarrow Ti(s) + 2MgCl_2(s)$$

$$\frac{1000g}{189.9} = 5.266$$

From this we can see that half of Mg moles ($\cancel{2}$ 2.057) is less than 1 mole of Ti. Hence Mg is limiting reagent

$$\therefore \frac{4.115}{2} \times \overset{47.9}{\cancel{189.9}} = \cancel{391}$$

$$= \cancel{400}\ 98.6g$$

Ideal Gas Equation

Avgadros Law → $V \propto n$

Boyle's → $V \propto \frac{1}{P}$

Charles's → $V \propto T$

$$\Rightarrow \underset{\text{volume}}{\overset{\text{Pressure}}{P V}} = \overset{\text{moles}}{n}\ \underset{8.31}{R}\ \underset{\text{Temp}}{T}$$

P = Pa

$V = m^3$

n = moles

R = 8.31

T = K

Assumptions

1) Gas molecules do not interact with each other

2) $V \neq 0$

PV = nRT but ~~$R = \frac{m}{V}$~~

$n = \frac{Mass}{Mr}$

~~$\frac{PV}{1} = \frac{mRT}{Mr}$~~

=

$$n = \frac{PV}{RT}$$

$$\frac{m}{Mr} = \frac{PV}{RT}$$

$$Mr = \frac{mRT}{P\cancel{V}}$$

$$Mr = \frac{\text{density}(g/m^3) \times R \times T}{P}$$

Changing the conditions (divide PV = nRT by factor that is changing + isolate changes on LHS)

PV = nRT → lets say that pressure is changed. However, n, R, T are constant. $\therefore P_1V_1 = P_2V_2$

PV = nRT → lets say that temperature is changed, $\therefore \frac{PV}{T} = n \times R$ hence $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\frac{V}{T} = \boxed{\frac{nR}{P}} \leftarrow \text{constants}$$

PV = nRT → lets say that volume is changed, $\therefore \frac{P}{\cancel{T}} = \frac{nRT}{V}$ $\therefore \frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{P}{T} = \frac{nR}{V}$$

$$\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$$

Back Titration

e.g What % of limestone is $CaCO_3$? 1g sample reacts with 100cm³ 0.2 mol/dm³ HCl. Excess HCl required 24.8 cm³ of 0.100 mol/dm³ of NaOH to be neutralised

$CaCO_3 + 2HCl \rightarrow CO_2 + H_2O + CaCl$ $HCl + NaOH \rightarrow NaCl + H_2O$

~~100cm³ × 0~~ 0.1dm³ × 0.2 mol/dm³ = 0.02 moles of HCl total

0.0248 × 0.1 mol/dm³ = 0.00248 moles of NaOH and HCl used in neutralisation

∴ 0.02 mol − 0.00248 mol = 0.01752 mol of HCl reacted with $CaCO_3$

$\frac{0.01752}{2} \times (40+48+12) = 0.876g$ of $CaCO_3$

$\frac{0.867}{1.000} \times \cancel{10} \times 100\% = 86.7\%$

Practise Questions [Calculations Allsorts]

3) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

$\frac{1000g}{56+48} = 9.62$ moles ×3

28.8 moles

× (12+16)

~~807~~ 806.0g

6) 0.004 mol/dm³ × 0.025

= 1×10^{-4} moles

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

5×10^{-5} moles of H_2SO_4

$\overline{0.002075}$

0.0241 mol/dm³

4) $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$

$\frac{8g}{104} = $ ~~0.0769 moles~~ 0.05

2(56) + (48)

× 2

= ~~0.154~~ 0.1

0.1~~54~~ × (26.98) = ~~4.15g~~ ~~2.698~~ 2.70

7) 0.0235 × 0.250 = 0.005875 moles of acid

0.005875 moles × 10 = 0.05875

~~0.05875 × 13.8~~

$\frac{13.8}{0.05875} = $ ~~235~~ 234.9

$n = \frac{13.8}{?}$

? n = 13.8

? = $\frac{13.8}{n}$

VIP → Mixtures form when substances combine without chemical interaction, homogenous, → same phase of matter; hetero is opposite

4

$\text{solid} \underset{\text{deposition}}{\overset{\text{subliminantion}}{\rightleftarrows}} \text{gas}$

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4) X has CHO only $M_r = 85$

0.43g

$\quad\quad 10 \quad 15$

$C_xH_yO_z + \cancel{?}O_2 \rightarrow 5CO_2 + 5H_2O$

~~CH_2O~~

$\left(\frac{1.10}{44}\right) \rightarrow 0.025$

$\frac{0.45g}{18} \rightarrow 0.025$

$12+2+16 = 30$

$1.1 + 0.45 - 0.43$

$C_5H_{10}O$

$1.1 + 0.02 = \underline{1.12}$

$\frac{1.12}{32} = 0.035$

5) $0.05 \times 0.250 = 0.0125$ moles

$0.1 \times 1\text{mol/dm}^3 = 0.1$ mols

$0.1 - 0.0125 = 0.0875$

$NH_4Cl + NaOH \rightarrow NH_3 + NaCl + H_2O$

$0.0875 \text{ moles} \times (14+4+35.5)$

$= 4.68125 \approx \underline{4.68}$

Hydrate Questions

- E.g: A sample has formula $K_2CO_3 \cdot xH_2O$. 10g.00g of it is headed and converted into an anhydrous salt, that was weighed and was found to be 7.93g

① Write Reaction

	$K_2CO_3 \cdot xH_2O\,(aq) \xrightarrow{heat}$	$K_2CO_3\,(s)$ +	$xH_2O\,(l)$
I	10g	0	0
C	-10g	+7.93 [0.05737mol] ?	
E	0	7.93g	

② Moles of K_2CO_3

$\frac{7.93g}{138.21} = 0.057376$ mole

∴ it is $K_2CO_3 \cdot 2H_2O$

∴ moles of $K_2CO_3 \cdot xH_2O = 0.057376$

$0.057376 = \frac{10g}{138.21 + 18x}$ ∴ $138.21 + 18x = 174.29$

$18x \approx 36$

$\underline{x \approx 2}$

② Atomic Structure Notes

Basics

Date No.

${}^{A}_{Z}X$ → A = Mass Number
X = element symbol
Z = Proton Number

Mass No: Total number of neutrons and protons
Proton No: Total number of protons in an atom

Isotope → an atom with a different number of neutrons than an atom of the same element ~~tk~~, but same proton + electr number. Diff physical but same chemical properties

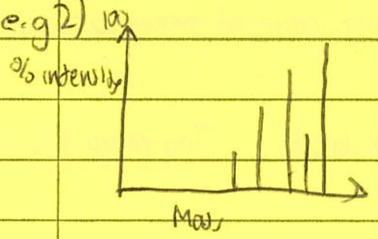
Isotopes

- → Different physical properties (e.g mass/density / rate of diffusion) because isotopes vary in mass
- → Same chemical properties ~~s~~ because electrons ~~de~~define chemical properties
- → Calculating Relative Atomic Mass

e.g 1) Rb has 72.1% of Rb-85 and 27.9% of Rb-87. Find the RAM of Rb

$$72.1\%(85) + 27.9\%(87) = \underline{\underline{85.5}}$$

e.g 2)



1) add up all % intensities
~~2)~~ ~~Divide each~~ mass~~by intensity~~ (sum of … es to)
2) Divide sum of masses by total intensity

Uses of Radioisotopes

1) Carbon Dating → C14 is in organic matter, number of C-14 atoms present ~~a~~ related to half life of C-14 will provide the age of the matter
2) Treating Cancer → Co-60 produces gamma rays. Can cause mutations and deaths of healthy ce
3) Tracing → I-125 is used to test thyroid activity. I-131 kills thyroid tissue

Mass Spectrometry

- → a tool that allow chemists to compare the masses of 2 different particles and measure ~~of it~~ the abundance of the particles

Electron shells

- → As you go up shells, energy increases, as the shells converge
- → Electrons in a shell = $2n^2$
- → Applying heat/electricity/light to an electron causes it to jump up to a higher shell of higher energy. After energy is lost, the electron moves down to its ground state (original shell), releasing energy as an electromagnetic wave (photon)

gap between shells non-existent

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→ If enough energy is applied, the electron goes to N ∞ (out of atom), ionising the atom in the process

First Ionisation Energy: Energy needed to remove 1 mole of electrons from a mole of an atom in gaseous state.

Factors affecting FIE

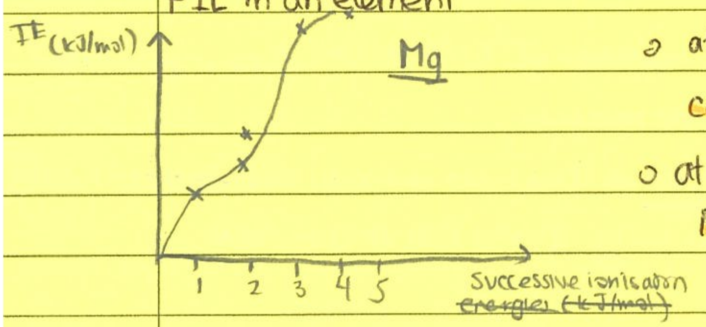
1) Number of protons → ↑ proton no, ↑ FIE because stronger forces of attraction hold the electron to be lost in place, hence more energy must be used to break the forces of attraction holding the electron in place

2) Distance from Nucleus, ↓ ionic radius, ↑ FIE, less dist from area of positive charge density (nucleus), hence forces of attraction increase, ∴ ↑ FIE

3) Shell that valence electron is in. ↑ n, ↓ FIE, more dist from area of positive charge density hence forces of attraction i~~ncrease~~ decrease, ↓ FIE

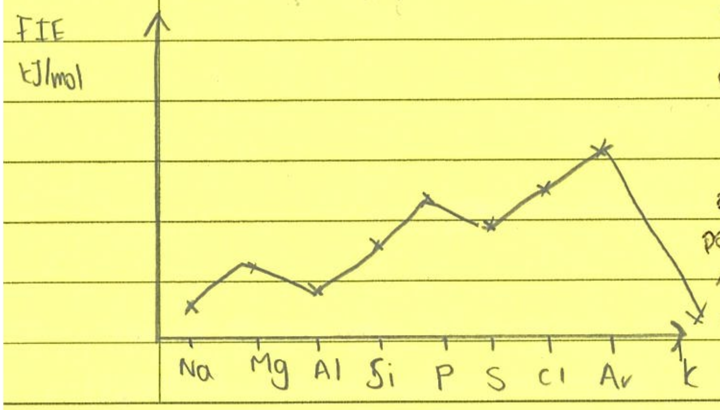
4) Shielding: Repulsive effect from electrons of same spin repelling each other. The more full shells you have, ↑ shielding, ↑ repulsion, ∴ ↓ FIE

FIE in an element



- at FIE (2) → increase because now electron removed from cation, ↑ attractive forces. Also ↓ ionic radius, ∴ ↑
- at FIE (3) → big jump because at n=2 now, lower energy level where electron closer to nucleus

FIE across Period 3



- C ... FIE
- Pr ... n nucleus, n=4 ↓ aff...
- De ... rther from positive nuc ... weaker
- De ... ectrons of sam...

Decrease at S because the p subshell have 3 electrons of the same spin that generate a repulsive effect on the electron to be lost, culminating in a reduced FIE

Drop at Al because ~~have~~ 1 e⁻ lost from p, further from nucleus, ↓ forces of attraction

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Calculating FIE

$E = hv$ ← frequency (1/s)
↑ energy ↖ Planck's constant (6.63×10^{-34})

$c = v\lambda$ ← wavelength
↗ 3×10^{8} ↑ frequency

only for FIE ↓

$$\boxed{E = \frac{hcl}{\cancel{v}\lambda}} = \frac{6.63\times10^{-34}\times3\times10^{8}\times6.02\times10^{2}}{\text{wavelength}}$$

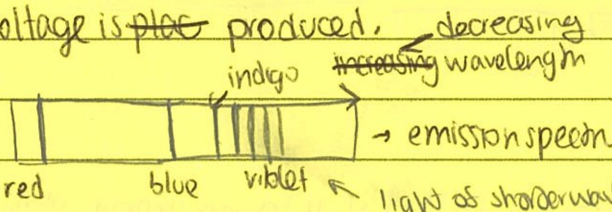
$$= \frac{\text{Planck}\times\text{speed of the flash}\times\text{Avogadr}}{\text{wavelength}}$$

Emission Spectrum / Absorption Spectrum

→ When electromagnetic radiation (clow) is passed through a collection of atoms, the electrons move to higher shells and when they return to ground state, varying electromagnetic waves are released and a spectrometer analyses it ~~back~~ relative to incident radiation (absorption spectrum produced)

→ hydrogen absorption spectrum
→ black lines on a continuous visible light ~~background~~ spectrum

→ When ~~to~~ white light is passed through hydrogen gas, an emission spectrum is produced when high voltage is ~~plac~~ produced.



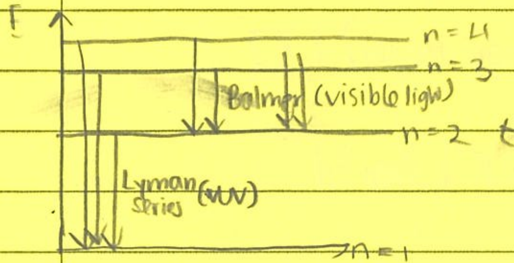
→ emission spectrum for H_2

→ black background with coloured, converging'n

↖ light of shorter wavelength converges due to increased photon energy

Made of ~~discreted~~ discrete lines, because the atoms are made of discrete energy levels and lines converge to the end, representative of the converging electron shells also because data is quantised

Lyman → anything to n=1
Balmer → anything to n=2

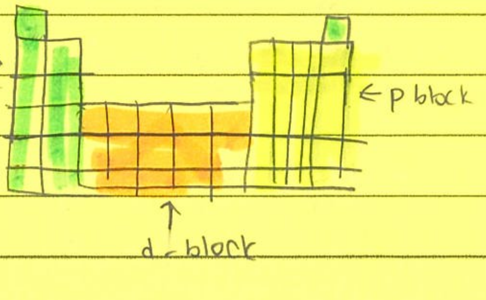


← lines converge because energy levels converge

Sublevels

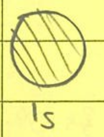
S – 1 orbitals
P – 3 orbitals
d – 5 orbitals
f – 7 orbitals

s block →

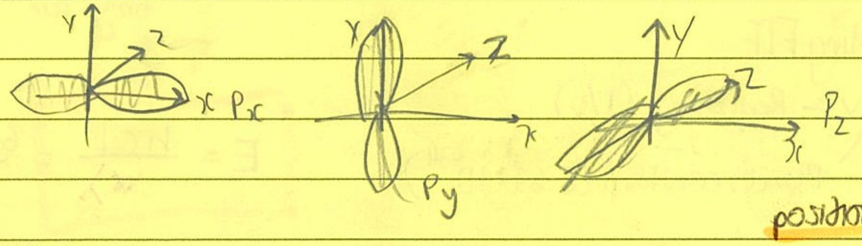


🟩 → elements where S is being filled
🟨 → elements with p orbitals being filled
🟧

S orbital



P orbitals



Principles

*1) Heisenberg's Uncertainty Principle → we cannot know both the speed or ~~condition~~ position of a body without changing one of those properties

2) Pauli Exclusion Principle – No 2 electrons can have the same quantum numbers, hence 2 electrons can be in the same orbital but have opposite spins

3) Hunds Law: For degenerate orbitals (equal energy), lowest energies are obtained, when the number of electrons having the same spin is maximised

4) Aufbau Principle: Electrons fill orbitals from lowest to highest energy levels.

Electronic Configuration

- In boxes with ↑ arrow representing +spin and ↓ arrow = −spin
- For Magnesium → $1s^2 2s^2 2p^6 3s^2$ or 1s [↑↓] 2s [↑↓] 2p [↑↓|↑↓|↑↓] 3s [↑↓] or Ne[$3s^2$]

For Oxygen → $1s^2 2s^2 2p^4$ → 1s [↑↓] 2s [↑↓] [↑↓|↑|↑] 2p

Exceptions

Copper is ~~4~~ [Ar] $4s^1 3d^{10}$ because a full d shell lowers energy, stabilising the atom. Chromium is [Ar] $4s^1 3d^5$ because all d orbitals have at least 1 electron, ↑ stability

Continuous vs ~~Discrete~~ Line Spectra

→ Continuous: contains all colours [wavelengths, frequencies energies] of VI

→ Discrete: quantised data

Note: transition metals ~~m~~ lose $\bar{e}$ from 4s first [higher E], then 3d

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A

③ Periodicity → reccuring trends in element properties, with increasing proton number

The table

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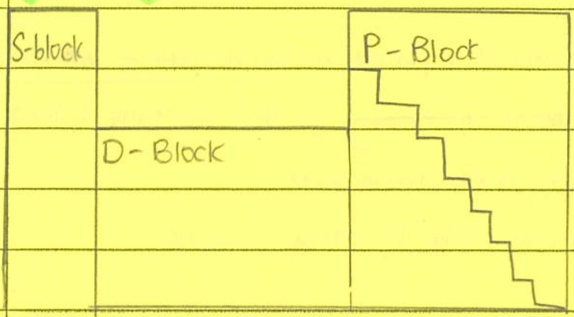


Properties of Metals

- Shiny + high m.p/b.p
- Sonorous
- ~~Malleble~~ Malleable
- ductile
- Good conductors of heat and electricity

Periodic Trends [Across Period 3]

1) Atomic Radius

→ The number of protons and valence electrons increase across the period

→ Hence, the attractive forces ~~hot~~ between the protons and valence electrons increases

→ As a result, the atomic radius decreases across a period because the attractive forces ~~holding~~ pull the shells towards the nucleus

2) Electronegativity (make reference to how shielding is similar)

→ definition: ability of an atom to attract a pair of electrons in a covalent to itself

→ Electronegativity increases across a period, as nuclear charge increases, due to a rise in proton number, hence so does the attractive forces between the element and the shared pair of electrons in the covalent pair

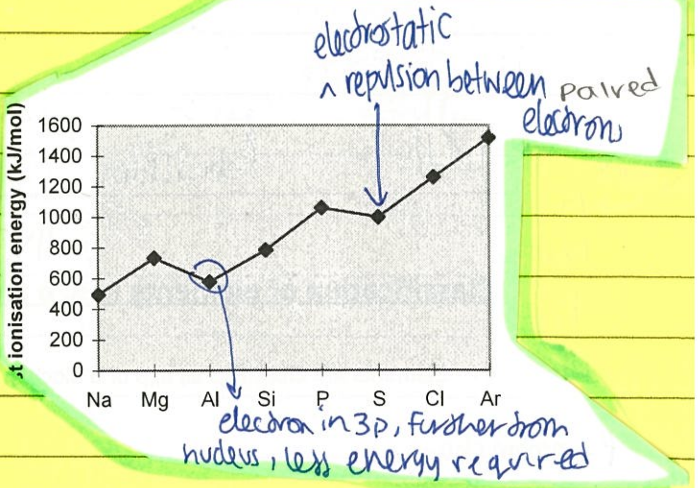
→ However, it decreases down the group due to decreasing effective nuclear charges [↑ shielding, atomic radius]

3) 1st ionisation energy

→ generally increases across period as the number of protons increases, hence the attractive forces holding the electrons in place increases.

→ When the 3p shell starts to get filled, the electron is further from the nucleus, hence less energy is required to remove it

→ There is a dip at sulfur because the p shell fills up for a second time, hence repulsive forces between electrons increase, decreasing FIE.



Node: Sulfur has lower FIE due to presence of paired electron

4) Electrical Conductivity

→ electrical conductivity of metals increases as you go across a period, as the number of valence electrons increases, hence there are more delocalised electrons ~~to carry~~ in the metallic lattice, hence there are more charged particles available to carry an electrical charge

→ in non-metals, there are no charged particles available to carry a charge

→ Si is slightly above 0 as it is a metalloid

5) M.P and B.P

Metals

→ More protons as you go across, ↑ attractive forces between delocalised electrons and protons in the nucleus

→ There will also be an increasing charge on the cations in the metal ~~that~~ lattice, hence the number of delocalised electrons increases and the attractive forces holding the lattice together increases

→ There is a jump in Si because it exists in a macromolecular structure, hence more bonds need to be broken.

Non-Metals (affected by ~~ma~~ size of elemental state)

→ lower m.p because they are simple covalent structures

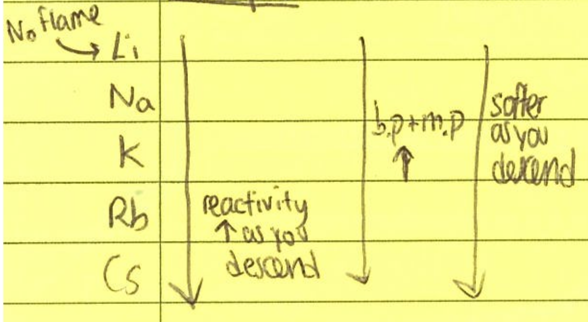
→ higher at S as it exists as S_8

→ P exists as P_4, hence 2nd highest

→ The larger the molecule, the stronger the Van der Waals forces holding the molecule together

✳ Periodic Trends

Group 1



✳ Reactivity increases as you descend because they react by losing their outer electrons to form their ion. The outer electron is in successively higher energy shells as you descend, where forces of attraction holding them together are weaker. Hence, less energy is required to remove it

Physical Properties
→ good conductors of heat and electricity
→ low densities

Chem Properties
→ reactive
→ form ionic compounds with non-metals

Reactions of P3 elements and Group I elements

Group I

$2Li(s) + 2H_2O(l) \rightarrow$ ~~2LiOH + H~~
$LiOH(aq) + H_2(g)$

$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

Magnesium with steam

$Mg + H_2O(g) \rightarrow MgO + H_2$

Across Table → alkaline oxides → amphoteric → acidic

Aluminium oxides

$Al_2O_3 + 6HCl \rightarrow$ ~~2ACl~~ $2AlCl_3 + 3H_2O$

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$

P3 Oxides with H_2O

$Na_2O + H_2O \rightarrow 2NaOH$

$MgO + H_2O \rightarrow Mg(OH)_2$

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

P3 elements with H_2O

$2Na + 2H_2O \rightarrow 2NaOH + H_2$

$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$

$Cl_2 + H_2O \rightarrow HCl + HOCl$

× Al → S do not react with H_2O

P3 elements with O_2

$4Na + O_2 \rightarrow 2Na_2O$
$2Mg + O_2 \rightarrow 2MgO$
$4Al + 3O_2 \rightarrow 2Al_2O_3$
↕ ionic

$Si + O_2 \rightarrow SiO_2$ (giant covalent)

$4P + 5O_2 \rightarrow 2P_2O_5$
$S + O_2 \rightarrow SO_3$
$4Cl_2 + 7O_2 \rightarrow 2Cl_2O_7$
↕ simple covalent

Halogens

	reactivity	b.p/mp	darker colour
F_2	↑	↓	↓
Cl_2			
Br_2			
I_2			

✳ Reactivity decreases as you ascend as the outer shell is increasingly at higher energy levels and further from the nucleus. This decreases the attractive forces that pull an electron into the valence shell of a halogen, decreasing its reactivity.

The halogens can displace less reactive halogens as the halogens that are more reactive are better oxidising agents, hence they gain electrons from the other halogen that they oxidise.

e.g i] $Cl_2(aq) + 2Br^- \rightarrow 2Cl^- + Br_2$

Phys Properties
→ coloured compounds

Tests

F^- very soluble ↑

Halide	+ $AgNO_3$	+ dilute NH_3	+ conc NH_3	+ $Pb(NO_3)_2$
F^-	colourless	~~NO~~ NIL ~~ppt redissolves~~	NIL ~~ppt dissolves~~	white
Cl^-	white	ppt dissolves ~~none~~	ppt redissolves	white
Br^-	cream	none	ppt redissolves ~~no visible~~	yellow
I^-	yellow	~~ppt redissolves~~ none	none	yellow

Noble Gases

- colourless gases
- Monoatomic
- very unreactive [because they cannot gain/lose electrons]

Do not form cations as they have the highest first ionisation energies

Do not form anions as extra electrons would have to be added to an empty outer energy level, where they would experience a negligible effective nuclear pull up.

Transition Metals

Definition: A metal that forms at least 1 stable ion with a partially full d-shell of electrons

Physical Properties

- high electrical and heat conductivity
- high m.p
- mallaeble / ductile
- high tensile strength

Chem Properties

- varying oxidation numbers
- coloured compound
- catalyst in elements / compounds

Atomic Radii

- There ~~has~~ is a relative decrease (small) in atomic radii across d-block due to a small increase in effective nuclear charge across the d block. The increase is small because the charge is largely offset by the addition of one electrons.
- The ~~similitary~~ similarity in atomic radii results in an ease for transition metals to form ~~tons~~ alloys

Why Zn is not a transition metal

- Zn only forms the 2+ oxidation state in its compound
- d shell is full in both ion and atom, hence it cannot be a transition metal as a transition metal ion has an incomplete d shell.

Why Transition Metals have varying oxidation states

1) When there is a large jump in ionisation energy, the ion that is formed after that jump is energetically unstable, hence it rarely exists.
2) The increase in ionisation energies are gradual for transitions metals as the 4s and 3d shells are close in energy. However, when the inner 3p electron is removed, the ion is energetically unstable due to a large jump in ionisation energy. Hence ~~as~~ as electron are being removed from 4s and 3d, stable ions are formed.

Notes on transition metals

→ all transition metals show 2+ and 3+ oxidation states but 3+ becomes less common as you go across a period because ↑ nuclear charge hence ↑ 3rd ionisation energy

→ Oxidation states above +3 show covalent character. Higher charge ions can polarise negative ions and increase the covalent character of the compound

→ ↑ oxidation, ↑ ability as a oxidising agent.

Examples of Metal Catalysts

→ V_2O_5 in contact process

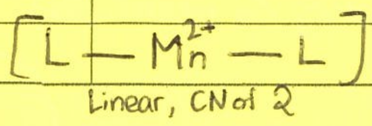
→ Fe in Haber Process

Coordinate bonds and ligands

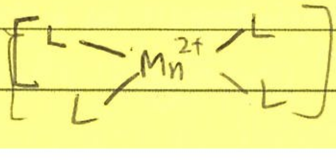
Transition metal ions in solution have a high charge density and as a result, they act as Lewis acids and attract species rich in electrons. These species are known as ligands, neutral molecules or anions that contain one or more non-bonding pairs of electrons. The ligands form covalent (dative) bonds with the central transition metal ion to form a complex ion. * represented by an arrow from ~~lewis~~ lewis base (a.k.a ligand)

A complex ion has a central metal ion at its centre with a number of other molecules surrounding it

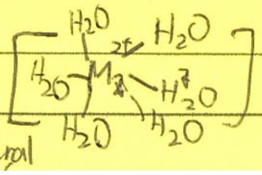
The number of coordinate bonds to one central ion is the coordination number



Linear, CN of 2



square plannar / tetrahedral
CN of 4



Octahedral

Examples of Ligand complex ions

Complex	Ligand	CN	Shape
$[Fe(H_2O)_6]^{2+}$	H_2O	6	octahedral
$[CuCl_4]^{2-}$	Cl^-	4	tetrahedral
cisplatin) $[Pt(Cl_2)(NH_3)_2]^{2+}$	Cl^- and NH_3		
MnO_4^-	O^{2-}	4	tetrahedral

Ligands can be replaced by other ligands

For example → $(CuCl_4)^{2-} \underset{+H_2O}{\overset{+Cl^-}{\rightleftharpoons}} [Cu(H_2O)_4]^{2+} \underset{NH_3}{\overset{+H_2O}{\rightleftharpoons}} [Cu(NH_3)_4]^{2+}$

If ~~so~~ a ligand is higher on the spectrochemical series than another, it can displace that ligand.

Polydentate Ligands → ligands that can utilise 2 or more pairs of unbonded electrons to form a ~~covalent~~ coordinate bond. Examples include oxalate ions $(COO^-)_2$ and EDTA and $EDTA^{4-}$ (EthyleneDiamineTetraAcetic acid). EDTA forms a hexadentate ligand as there are 6 ~~unpa~~ unbonded pairs of electrons available in a single molecule of EDTA. For example, the coordination number of $[Cu(EDTA)]^{2-}$ is 6 as 6 bonds are made to the central metal ion.

Magnetism

→ every single spinning electron can behave as a small magnet

→ Electrons with opposite spins (paired electrons) have opposing orientation and hence ~~cancel the~~ have no net magnetic effect

→ Types of Magnetism

Ferromagnetism → metals like Fe, Co and Ni are ferromagnetic. Their unpaired ~~d~~ electrons line up with parallel spins in regions called domains, irrespective of whether an external electric or magnetic field is present. Ferromagnetism is permenant magnetism

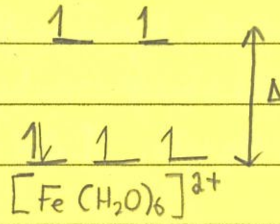
Paramagnetism → paramagnetic metals contain unpaired electrons, each of which create a small magnetic field and will line up in domains when an electric or magnetic is applied. This makes the complex weakly magnetic ~~as~~, reinforcing the external field.

↑ number of unpaired electrons, ↑ paramagnetic effect

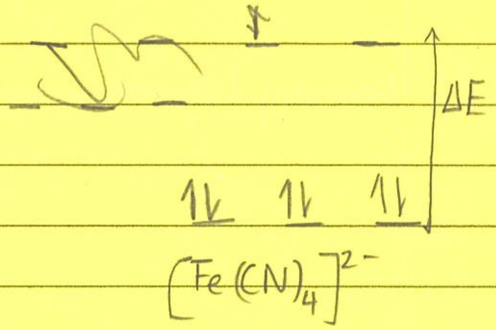
Diamagnetism → when all electrons in a complex are paired

Iron ligands $\boxed{{}^{5}Fe}$

- → can be dia or paramagnetic
- → d orbitals are split by ligands
- → ↑ position of ligand on series, ↑ ΔE (↑ splitting)
- → if low ligands like H_2O are used (fig 2.1), electrons can occupy all d orbitals, leaving 4 unpaired electrons, a.k.a 4 units of paramagnetism



- → if higher ligands like CN^- are used, higher splitting is observed, hence only lower d orbitals will be occupied with no unpaired electrons, making it diamagnetic



Coloured complexes

The colour of transition metal ions can be related to the ~~presen~~ presence of partially filled d orbitals. The ion Sc^{3+} is colourless as a complex ion because its 3d block is empty. Zn^{2+} is colourless because the 3d shell is full.

Ligands have the ability to split the d orbitals into 2 sub levels

The d orbitals in a isolated transition metal atom or ion, the d-orbitals are degenerate as they contain the same amount of energy. When a complex ion is formed with a ligand, the ligands act as Lewis ~~bases~~ ~~acids~~ bases and donate a pair of non-bonding electrons to form a coordinate bond. As the ligands approach the d orbitals along the axis, the ligand electrons will repel the $d_{x^2-y^2}$ and d_{z^2} orbitals as they lie on the axis. As a result, the d orbitals are split, 2 to higher energy, 3 to lower energy. This difference in energy (ΔE) corresponds to the wavelength of light absorbed. ($\Delta E = h\nu$) ($c = \nu\lambda$). Using the colour wheel, we can see what wavelength of light is ~~emitted~~ transmitted

The frequencies of light absorbed by e^- as they move from lower to higher are complementary to absorbed

Factors affecting the colour of a complex ion

Date No.

1) Nuclear charge
→ ↑ protons, ↑ effective nuclear charge
→ This increases the electrostatic attraction between the donated pairs of electrons and the nucleus
→ Hence, ΔE is higher, resulting in a higher wavelength of light being ~~emitted~~ transmitted

2) Ligand identity
→ The higher the ligand on the spectrochemical series, the higher the charge density
→ The higher the charge density, the higher the split in the d orbitals, because ↑ repulsion with orbitals
→ The higher the split, ↑ ΔE

3) Geometry / Stereochemistry

4) Oxidation states of the metal ion
→ ↑ oxidation state, ↑ charge, ~~↑~~ ↓ number of electrons
→ ↑ electron repulsion between the ligand and d electrons
→ hence ↑ ΔE

Alkali Metals with water

Li → floats, no flame, effervescence
Na → floats, flame produced [orange flame], as lower b. m.p
K → Faster than Na, lilac flame
Rb → dense ∴ sinks

} all form alkaline solution

Chapter 4: Bonding

Ionic bonding → an ionic bond is the electrostatic attraction between 2 oppositely charged ions

→ Ionic compounds are formed when electrons are transfered from one atom to another to form atoms with a complete outer shells of electrons

→ Example (formation of NaCl) → formed when Na burns in chlorine, the energy from the heat breaks the bonds in the Cl_2 molecule to give Cl atoms. Each sodium atom then transfers one electron to each chlorine atom to form Na^+ and Cl^-

Polyatomic ions

1) hydroxide, OH^-
2) Nitrate, NO_3^-
3) Nitrite, NO_2^-
4) sulfate, SO_4^{2-}
5) hydrogensulfate, HSO_4^-
6) carbonate, CO_3^{2-}
7) hydrogencarbonate, HCO_3^-
8) ethanoate, CH_3COO^-
9) Phosphate, PO_4^{3-}

Ionic bonds form due to high electronegativity differences (>1.8)

Properties

1) Exist in a crystal lattice structure
2) High m.p and b.p → due to strong electrostatic forces of attractions between ions, hence large amounts of energy are required to melt ionic compounds
3) Low volatility → ionic compounds have low odours, because of high lattice enthalpies
4) Soluble in polar compounds – The δ^- part of a polar molecule attracts the cations in a ionic lattice and the δ^+ part attracts the anions. This causes the ions to seperate from the lattice and become surrounded by polar molecules. If water is the polar compound, the ~~ionic~~ ions have been hydrated, otherwise, they have been solvated
5) Conduct electricity in liquid and aq form → In solid state, ~~comp~~ ions are held in place within the lattice and cannot move to carry a charge. In liquid and aq forms, the ions are free to move and carry a charge
6) Brittle – Movement of ions within the lattice places ions of the same charge alongside one another, hence the repulsive forces cause them to split.

Octet Rule: Atoms tend to get valence shell
of 8 electron, exception
include Be and B

1 Covalent Bond: Electrostatic attraction between a shared pair of electrons and positive nuclei

Covalent Bonding

Date No.

→ sharing of one or more pairs of electrons so each atom involved achieves noble gas configuration

→ The formation of a covalent bond stabilises the atoms, so energy is released as the bond forms

→ tendency of atoms to form a stable arrangement of 8 outer electrons is called the octet rule

→ double and triple bonds can be formed e.g O=O and N≡N

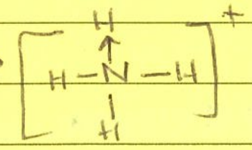
→ If you have more bonds (double bond vs triple bond), the bond length is shorter and the bond is stronger

Shorter the bond, the more powerful it is.

- Multiple bonds have a greater number of shared electrons and so have a stronger force of electrostatic attraction between bonded nuclei
- Hence, there is a greater pulling force on the nuclei, bringing them closer together

Coordinate (dative) covalent bonds

- a ~~co~~ covalent bond in which both electron in the covalent pair originate from the same atom.
- E.g NH_4^+ →



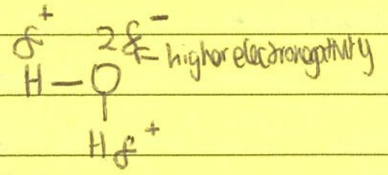
Polar Covalent Bonds

→ polar bonds result from unequal sharing of electrons

→ The more electronegative atom exerts a greater pulling power on the shared electrons, hence it holds the electrons more than the other, ~~but~~ and now electron distribution is unsymmetrical.

→ This is because one end of the molecule becomes more electron rich than the other.

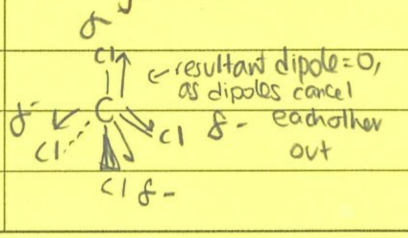
e.g →

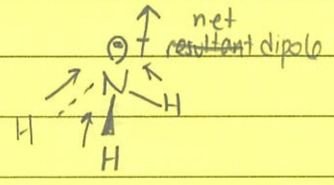


↑ electronegativity difference, ↑ polarity

→ The more electronegative atom has the greatest electron density when bonded

Determining Net dipole





Van Der Waals Forces = collective term
for LDF, permenant → instaneous dipole,
and p.dipole → p.dipole 3

Date No.

Intermolecular Forces

London dispersal forces [LDF]

In non polar molecules, electrons are unevenly spread throughout the molecule but can be concentrated ~~in~~ at the sides of the molecule, producing a temporary instantaneous dipoles. These dipoles can ~~produ~~ induce another dipole in a neighbouring particle, resulting in weak attraction between the particles. (by way of polarising the other molecule

Factors affecting LDF

1) ↑e^-, ↑ LDF because more electrons produce stronger dipoles
2) ↑RMM, ↑LDF because larger ~~te~~ instantanous dipoles created
3)

Dipole – Dipole Forces

Polar molecules are attracted to each other because the more electronegative elements attract the least electronegative element. Positive end of one molecule attracts the negative end of another molecule.

$$\overset{\delta+}{I}-\overset{\delta-}{Cl}\ \text{''''''}\ \overset{\delta+}{I}-\overset{\delta-}{Cl}$$

↑
dashed line represent weak intermolecular forces

Hydrogen bonding $\boxed{H}$

→ occurs when H is bonded to a small, highly electronegative element (e.g O, N, F)
→ The electron pair ~~moves~~ is attracted to the more electronegative element, leaving a single proton in the hydrogen
→ The proton then attracts a non-bonding pair of electrons from the ~~e~~ highly electronegative element, creating a stronger dipole – dipole attraction.

Proof of hydrogen bonding

A graph of hydrogen compounds against temperature shows that if you go down a group, the b.p increases because more electrons are used in forming dipole-dipole forces. However the first element hydrogen bonds with in a period, its compound has an ~~unus~~ unusually high b.p, showing that additional intermolecular forces of attraction are present; forces that require more energy to break

Intermolecular forces in terms of bond strength

valent > hydrogen bonding > dipole-dipole > LDF

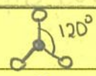
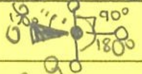
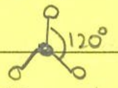
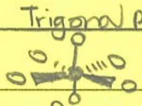
The weaker the intermolecular forces, the lower the boiling point.

*c reading at the end

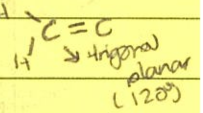
* Valence Shell Electron Pair Repulsion (VSEPR) theory

→ theory states that pairs of electrons arrange themselves ~~so~~ around the central atom such that they are as far apart as possible minimising forces of repulsion between pairs

→ Repulsive forces → l.p − l.p > b.p − l.p > b.p − b.p (b.p = bonded pair) (l.p = lone pair)

Total no. of e^- pairs	b.pairs	l.pairs	shape + example
2	2	0	 linear, e.g $BeCl_2$, 180°
3	3	0	 trigonal planar, e.g BF_3, 120°
	2	1	 bent, e.g SO_2, 118°
4	4	0	 tetrahedral, e.g CH_4, 109.5°
	3	1	 trigonal pyramid, e.g NH_3, ~~704~~ 107°
	2	2	 bent, e.g H_2O, 104.5°
5	5	0	 trigonal bipyramidal, e.g PF_5, 180°, 90°, 120°
	4	1	 distorted tetrahedral, 118°, 89°
	3	2	 or  e.g ICl_3 Trigonal Planar T-shape
6	6	0	 octahedral, 90°, SF_6
	5	1	 distorted square pyramid, 89°, IF_5
	4	2	 square planar, 90°, XeF_4

For molecules like C_2H_4, look at only one C atom e.g



Note: Electron Domain Geometry (EDG) describes shape formed by total number of electron domains. Moleceluar geometry is actual shape formed

Explaining ~~H~~ how VSEPR gives a shape

→ Shape is created because it minimises the repulsive forces between the X lone pairs/and Y ~~lone~~ bonded pairs, and which pairs repel most

→ E.g H_2O has a bent linear shape because it minimises the repulsive forces between the 2 lone and 2 bonded electron pairs. The lone pairs repel each other more than the bonded pairs ~~do~~.

→ Lone-lone pair equal repulsion

Allotropes of Carbon

- Allotropes occur when an element can occur in different crystalline forms
- Diamond is a strong form of carbon as each C is covalently bonded to 4 other Cs, forming a macromolecule. All electrons are localised, so it cannot carry a charge.
- In graphite, each C has 3 strong covalent bonds to 3 other C atoms to give layers of hexagonal rings. The layers can slide over each other, hence graphite is a good lubricant. Because the electrons are delocalised, graphite can conduct electricity
- Graphene is 1 atom thick graphite that is a semiconductor, light and is 200x stronger than steel
- C_{60} - Buckminsterfullerene → football looking structure → sp^2 hybridization; semiconductor because only small number of delocalised electrons

Resonance Structures [e.g C_6H_6, CO_3^{2-}, O_3]

→ Sometimes, a molecule can have many potential Lewis structures, and if none of them are stable, the molecule must keep moving between the potential structures because it moves the negative charges around stabilising itself in the process.

→ Eg in a double bond, (2 O and 1 C) each have a p orbital with one electron left after σ bonds have been formed. Instead of just forming one double bond (C=O), the electrons delocalise over all 3 atoms, something that is more energetically favourable than forming a single double bond, hence the double bond can be in a variety of locations

→ electrons from the π bonds [p electrons] delocalise + spread evenly over possible bonding sites, shared across different bonding zones

Formal Charge

→ assumes all atoms have same electronegativity

→ FC = VE − BE (of the atom) − LE (lone electrons)

e.g $O=C=O \rightarrow 6-2-4=0$ $\quad 4-3-1=0$

$4-4-0=\underline{0}$ vs $|O\equiv C-\bar{O}|$

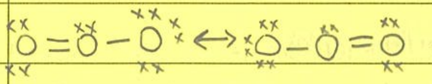
$6-3-2$
$=1+$

→ The structures that are most likely are those that have the least charge transfer (lowest charge per atom), hence it is the most stable arrangement

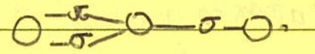
→ ~~Bc~~ More stable is negative charges on most electronegative element

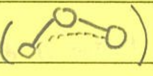
FC = VE - BE - NBE

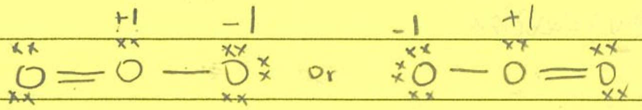
Ozone

 → The central O atom has an electron domain geometry of 4, but its molecular geometry is bent (117°) due to the presence of a lone pair.

Because there are a total of 3 pairs of electrons employed in bonding, the bond order of ozone is 1.5.

 The electrons in the π bond are not held tightly and are delocalised, giving rise to resonance structures.

It's true structure is a resonance hybrid. () Ozone is also polar, despite the fact that it is made ~~of~~ only of O atoms. This can be explained using formal charge



The uneven distribution of electrons through the molecule, as illustrated by formal charge results in a net dipole accross the molecule, making it polar.

The Ozone Layer (in the lower stratosphere)

- → contains 90% of the atmosphere's ozone
- → A cycle is used to maintain ozone levels, involving the formation and breakdown of ozone and oxygen

$O_2(g) \xrightarrow{\lambda < 242nm} \overset{\text{(high E)}}{}2O^{\circ}(g)$ = oxygen radicals are produced, atoms that are highly reactive, due to the presence of an unpaired electron.

$O^{\circ} + O_2 \rightarrow O_3$

or

$O_3(g) \xrightarrow{\lambda < 330nm \text{ (low E)}} O^{\circ}(g) + O_2(g)$

$O_3 + O^{\circ} \xrightarrow[\text{slow}]{} 2O_2$

The energy needed to break down O_2 is higher than O_3 because of the difference in bond enthalpies (bond order 2.0 vs 1.5). Ozone absorbs radiation between 200nm to 315nm, such as UV-B and UV-C rays that can damage tissue. This absorption of radiation is also a major source of heat in the stratosphere, hence ↑ °C with increasing stratospheric height.

Catalysis + Ozone destruction by CFCs and NO_x

→ high ~~UV~~ energy UV rays results in the homolytic fission of the C-Cl bond to produce Cl°s.

→ C-F bond cannot be broken by UV rays but C-Cl can because the bond enthalpy is lower

→ Cl° break down O_3 and regenerate more radicals in the process, such that ozone can be continously broken down until the radicals escape or terminate ( )

→ $CCl_2F_{2(g)} \rightarrow CClF_2^{\circ}(g) + Cl^{\circ}(g)$ [~~radicle~~ radical initiation]

$Cl^{\circ}(g) + O_3(g) \rightarrow ClO^{\circ}(g) + O_2(g)$

$ClO^{\circ}_{(g)} + O^{\circ}(g) \rightarrow Cl^{\circ}_{(g)} + O_2(g)$ [propogation of radicles]

Evidence that supports this mechanism of reactions → ↑ ClO concentration, ↓ O_3 concendration

NO_2's ability to break down O_3

$$NO_2(g) \xrightarrow[\text{in UV}]{} NO + O^{\circ}$$

$$O^{\circ} + O_3 \rightarrow 2O_2$$

The catalyst can then be regenarated

Q°) $NO + O_3 \rightarrow NO_2 + O_2$

Overall

$$2O_3(g) \xrightarrow{NO_2(g)} 3O_2$$

Molecular Orbitals

→ formed when 2 atomic orbitals, each containing one electron overlap, forming a molecular orbital that is at a lower energy level.

→ σ (sigma) bonds are formed when s and s overlap, s and p overlap, hybrid orbital and s overlap, hybrid orbitals and hybrid orbitals and when 2 p orbitals overlap head on on the internuclear axis

→ π bonds are formed when 2 p orbitals overlap sideways on. This bond only forms alongside the formation of a σ bond, it also occurs above and below the internuclear axis

Double + Triple Bonds

Double bonds consist of a σ and π bond, the ~~no~~ atoms involved have been sp^2 hybridized

Triple bonds consist of 2 π bonds and 1 σ bond, indicating sp hybridization.

The π bond overlap is not as strong as the σ bond ~~because~~ as evidenced by the decolourisation of bromine by ethene (breaking the π bond in C=C)

8

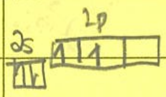
Hybridization : merging of atomic orbitals within the same atom

Degenerate orbitals

o.

sp³

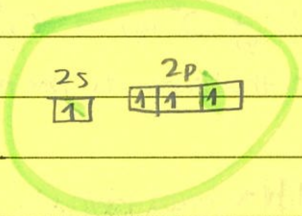
Carbon as an example



→ carbon can only form 2 bonds in this state, since only 2 unpaired electrons are available

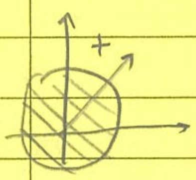
Since there is a small energy gap between 2s and 2p, energy can be provided from the C atom to promote an e⁻ from 2s into the vacant 2pz orbital! Now C can form 4 bonds! This is energetically favourable as when bonds are made later, energy will be released and the system will stabilise.

s there
re 4
npaired
electrons ↖

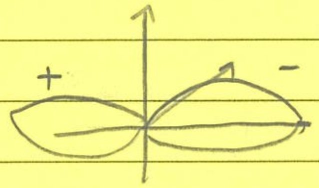


→ merging of 3p orbitals and one s orbitals

S orbital



p orbital (px)

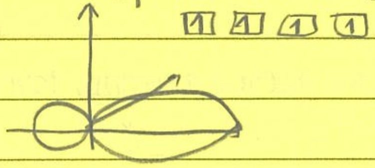


→ The positive s attracts the negative part of p, forming an sp³ orbital (4 variants)

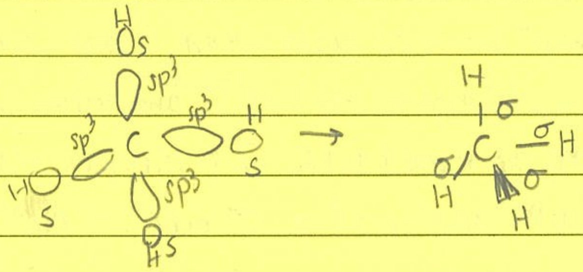
→ The orbitals arrange themselves in a manner such that repulsion between them is minimised

→ formed when ~~molecule~~ electron domain geometry = 4. Tetrahedral shape (109.5°)

sp³ orbital



CH4



sp^3 → ~~4~~ bonds that have no double

sp^2 → must have a double bond

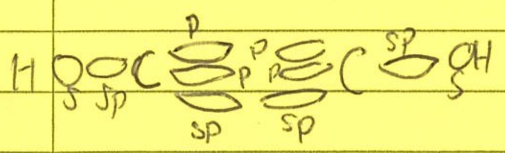
sp^1 → 2 double bonds or a ~~single~~ triple bond

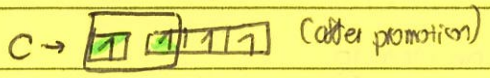
sp^1

→ when EDG = 2 domains

C_2H_2

$H-C\equiv C-H$





↓ these 2 orbitals merge to form 2 sp orbitals

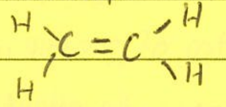
2 π bonds are formed and 1 sigma bond is formed between the Cs.

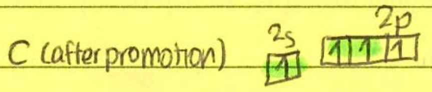
Predicting bonding through hybridization

sp^2

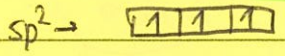
→ EGD = 3 domain

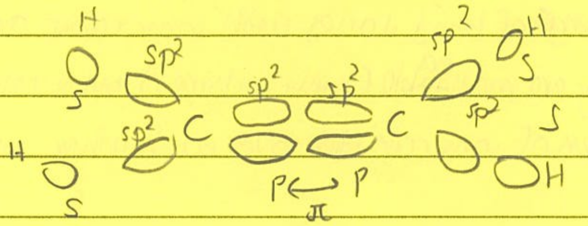
C_2H_4

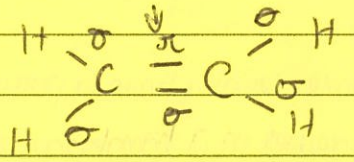




Only 2 of the p orbitals merge with the s, to form 3 sp^2 orbitals







The extra p orbitals overlap sideways on to form a π bond

Carbon

	Graphite	Diamond	C_{60}
Structure	Each C is sp^2 hybridized, hexagonal rings, held by LDF, 120° layers	Each C is sp^3 hybridized, 109.5°, ~~LDF~~ covalent	sp^2 hybridized, football-like structure
Conductivity (e^-)	1 e^- delocalised per C atom, hence can carry charge	No delocalised charged particles	Some e^- mobility, semiconductor
Special properties	slippery because layers can slide over each other	Very hard, high m.p	low m.p, very light + strong

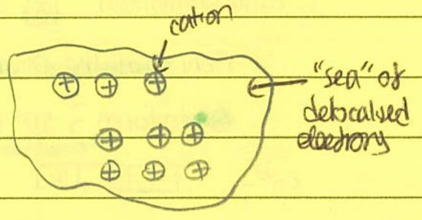
Alloys: added metals have different charge and radius, distort structure of original metal such that non directional bonding occurs.
→ less ductile + malleable, due to distorted structure
→ e.g solder alloy melts at lower temp, suitable for welding
tin + lead

Date No.

Metallic Bonding

In a metal, valence electrons delocalise from individual atoms, such that metals consist of a closely packed lattice of positive ions surrounded by delocalised electrons.

A metallic bond is the attraction that 2 neighbouring cations have for the delocalised electrons between them.



Strength of bond varies with ionic radius and ion charge

They are malleable (bent + reshaped) and ductile (can be drawn into wires) because the layers of ions can slide over each other without breaking more bonds that are made.

Solubility

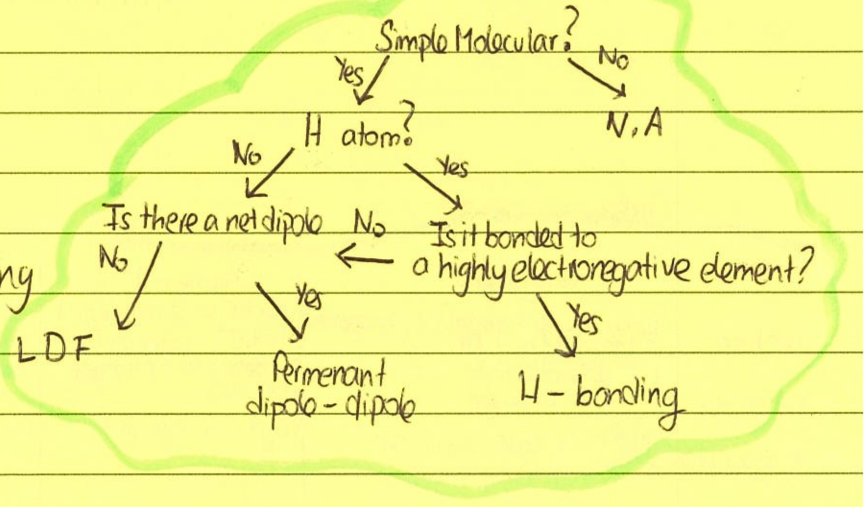
Organic molecules usually have a polar head and a non polar carbon chain. As the carbon chain length increases in a homologous series, the solubility decreases

CH_3OH
C_2H_5OH
C_3H_7OH
↓ decreasing solubility but ↑ melting + b.p

Non-polar substances dissolve in ~~the~~ other non polar substances easily because of the formation of LDFs between solute and solvent

M.P and B.P

- H-bonding > D-D > LDF
- ↑ Mr, ↑ strength of LDF and D-D
- Mr ~~m~~ creates greater change than replacing with electronegative element



Energetics - Chapter 5

Characteristics of Reactions

Exothermic → making bonds, rise in external temp, $-\Delta H$
→ energy released by product bond formation > energy used to break reactant bonds

Endothermic → breaking bonds, decrease in external temp, $+\Delta H$
energy released by forming prod bonds < energy used to break reactant bonds

~~Calir~~
Calorimeter problem
→ incomplete combustion
→ heat supplied to calorimeter itself / some heat lost to environment

Systems

Open: Chemicals + energy can be transfered between systems and surroundings

Closed: Only energy transferred between system + surroundings

To improve calorimeter, better insulation, abundant O_2 and etc

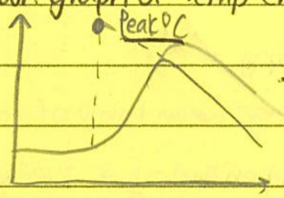
Calculating enthalpy change (kJ/mol)

$$q = \frac{\text{mass} \times \text{SHC} \times \Delta\text{temp}}{\text{moles of } \cancel{\text{wh}} \text{ limiting reagent}}$$

$$q = \frac{\boxed{m} c \Delta T}{\text{moles}}$$

mass of the water or medium through which T change is observed

If shown graph of temp change do the following



= line from decay rade

Definitions + Things to know

ΔH_r ⊖ ← standard conditions [100kPa, 1 mol/dm³, all substances in standard state]
r ← reaction type

1) $\Delta H_r^{[\ominus]}$ → enthalpy change when a reaction occurs in stated molar quantities, under (standard condition
2) $\Delta H_f^{\ominus}$ → Standard enthalpy change when ~~reaction~~ 1 mole of substance is formed from atoms of element
3) $\Delta H_c^{\ominus}$ → standard enthalpy change when 1 mol of fuel is combusted completely in excess oxygen
4) $\Delta H_{latt}^{\ominus}$ → standard enthalpy change when 1 mol of solid ionic ~~rg~~ crystal ~~in star~~ is broken into gaseous ions.
5) $\Delta H_{atomisation}^{\ominus}$ → When 1 mol of atoms in gas state are formed from element standard state
6) $\Delta H_{dissassociation}^{\ominus}$ → when atoms ~~is~~ are formed in gas state from 1 mole of the element in standard state
7) $\Delta H_{ionisation}^{\ominus}$ → enthalpy change when 1 mol of gas ions lose 1 mol of electrons to form 1 mol + ions gas
8) $\Delta H_{electron\ affinity}^{\ominus}$ → enthalpy change when one mole of atoms in gas state gain 1 mol of electrons to form 1 mol of gaseous anions
9) $\Delta H_{hydration}^{\ominus}$ → energy change when 1 mole of gaseous ions dissolves in sufficient H_2O to give an infinotely dilute solution

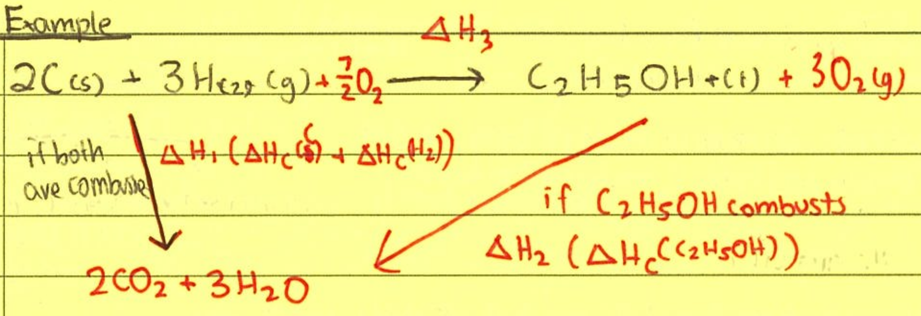
Note, if you reverse a reaction, sign on ΔH changes

~~W~~ Hess' Law

→ total enthalpy change of reaction is independent of route taken

→ neccessary if slow reaction, high activation energy, temp changes make reaction non standa

Example



Using vectors = $\Delta H_3 = \Delta H_1 - \Delta H_2$

$= 2\Delta H_c(C) + 3\Delta H_c(H_2) - \Delta H_c(C_2H_5OH)$

$= \underline{\underline{-273 kJ/mol}}$

Bond Enthalpy

→ Energy change when 1 mole of covalent bond in gas is ~~con~~ fa broken/formed

→ Average bond enthalpy → average energy change when one mole of covalent bonds in gas state are broken under ⊖ conditions.

→ Bond breaking = endo, forming = exo

If the products have more energy than reactants, the reaction is endothermic

$\sum$ bond enthalpies in ~~products~~ reactants − $\sum$ bond enthalpies in ~~reactants~~ products = ΔH_r

→ If you have an equation like this = $C_6H_{10}(l) + H_2(g) \rightarrow C_6H_{12}(g)$
the use of average bond enthalpies (ABE) are not suitable as 2 of the chemicals involved are in liquid form, and ABE refers to gas forms. If the latent heat of vaporisation is subtracded from the ΔH_r calculated by ABE

→ Average → ∴ no account of neighbouring atoms → why different from experiment

Energy Cycles

Lattice Enthalpy → measure of strength of electrostatic forces of attraction between ions in an ionic solid

Factors affecting $\Delta H_{latt diss}$

1) Ionic charge - The higher the charge on ~~atoms~~ ions involved, the stronger the electrostatic force of attraction between ions in the ionic solid. Hence, more energy is needed to break the forces of attraction ∴ $\Delta H_{latt diss}$ rises

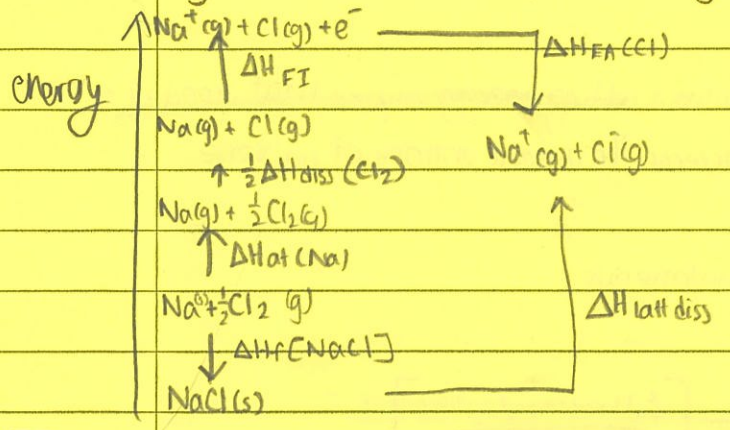
2) Ionic radius - The larger the ionic radius, the further the outer shells are from the positively charged nucleus ~~because~~, ~~dx~~ hence the electrostatic forces of attraction between ions are weaker, therefore ↓ ΔH_{latt}

Theoretical calculations assume molecules/ions are perfectly spherical with only 1 type of attraction [e.g electrostatic for ΔH_{LE}]

3

Born-Haber Cycles → [when y axis = energy]

e.g $NaCl(s) \rightarrow Na^+_{(g)} + Cl^-(g)$



$\Delta H_{latt\,diss} = \Delta H_{EA}(Cl) + \Delta H_{FI}(Na) + \frac{1}{2}\Delta H_{diss}(Cl_2)$
$+ \Delta H_{at}(Na) - \Delta H_f(NaCl)$

Solubility Reactions

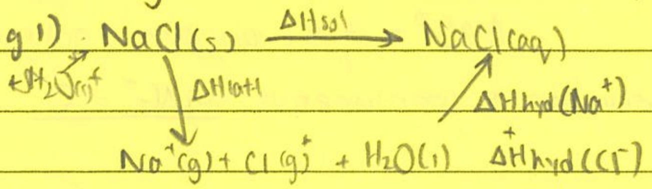
$\Delta H_{latt\,diss} + \Delta H_{hyd} = \Delta H_{sol}$

ΔH solution = enthalpy change when 1 mole of solute dissolves in an infinitely dilute solution of water under standard conditions.

Why infinitely dilute? → if small volume of water used, ions would just stick together

For something to dissolve, the overall ΔH sol should be exothermic

e.g 1)



Since ΔH hydration is always −ve and |ΔH lat| is always less than |ΔH hy| for a solution to form

The higher the ionic charge on ions, ↑ |ΔH hyd| since for stronger favourable ~~dipoles~~ intermolecular fo formed between solute + solvent. The smaller the ion radius, the stronger the forces, therefore, ↑ |ΔH|.

Entropy Change

Entropy (S) → distribution of available energy amongst particles

[s < l < aq < g] - states ordered in increasing entropy, as movement of particles increases as you go across hence more ways to distribute energy, ↑ entropy

The more particles there are (e.g more moles of products than reactants), the more ways there are to distribute energy, as there are more possible configurations for atoms. ↑ entropy

The more complex a molecule is, the higher its entropy because molecules with more bonds can move around in 3D space → more ways to distribute entropy ∴ ↑ entropy

Bear in mind that spontanuity is a yes no, not continous

$\Delta S^\ominus_r$ → J / Kelvin mole → remember to change to kJ

Entropy Change → Difference in entropies of products and reactants

Spontaneous Reactions: reactions that occur without adding energy beyond that needed to overcome activation energy barrier. They increase the overall entropy of universe

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$

↓ if ΔS_{total} is positive, the reaction is spontaneous

$$\Delta S_{surr} = \frac{-\Delta H_{system}}{T}$$

$$\therefore \Delta S_{total} = \underset{\uparrow}{\Delta S_{system\ or\ reaction}} - \left[\frac{\Delta H_{reaction/system}}{T}\right]$$

~~convert to kJ/mol K~~

ΔH	ΔS	ΔS total
−	+	+ve
−	−	+ve at low temperatures [↑ ΔSsurr]
+	+	+ve at high temperatures [↑↓ ΔS surr]
+	−	Never +ve

ΔG takes into account direct entropy change from chemical reaction and the indirect entropy change of the surroundings because of heat loss/gain

Gibbs Free Energy Change

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$\Delta G^\circ = -T\Delta S^\ominus_{\cancel{tot}\ system}$

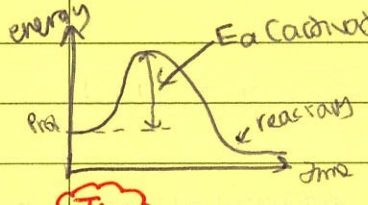
At $\Delta G^\ominus$ = −ve, reaction is spontaneous

At ΔG° = +ve, reaction is not spontaneous

To find temperature at which reaction is spontaneous, set $\Delta G^\circ = 0$

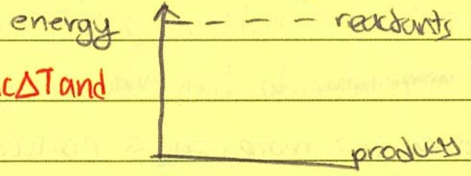
~~Ozone + Oxygen~~ If a reaction requires extra energy to start, could be high activation energy or insufficient energy to react at stated temperature.

For exo/endo



Activation energy - energy needed to break the bonds in reactants

Enthalpy Level Diagram ~~for~~ - ΔH



Tips

- → if asked for heat evolved, use $q = mc\Delta T$ and give in J / kJ
- → "Explain ΔS sign" → state and compare with reaction, e.g $2NH_3 \rightleftharpoons N_2 + 3H_3$, +ΔS because more moles of gas in prod than reactants
- → Remember to divide if you have to multiply!

Chapter 6 - Kinetics

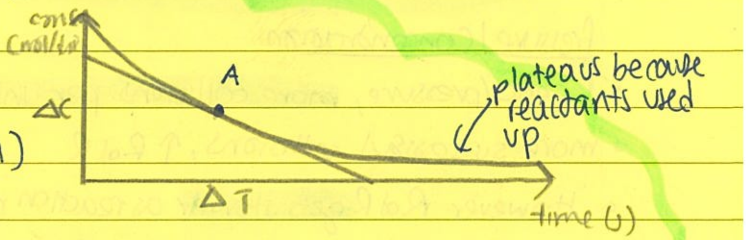
Rate of Reaction [must be +ve]

Def: change in concendration of products/reactants per unit time [$mol\,dm^{-3}s^{-1}$]

- can be monitered through vol of ⓘ gas evolved, mass change, colour change (clock experiment), pH changes, colour change (use of spectrometer to measure colour absorption)

Finding Rate of Reaction at given points on a graph

1) plot data onto graph
2) $\frac{dy}{dx}$ of graph = to rate of reaction
3) Draw tangent to curve at given point (e.g A)
4) $\frac{\Delta C}{\Delta T}$ = Rate at ~~gr~~ A (instaneous R of R)



plateaus because reactants used up

Note: initial R of R is at $x=0$

E_A = minimum amount of energy that particles need to collide successfully leading to reaction

Note that K.E (kinetic energy) of particles is directly proportional to temperature (Kelvin)

Collision Theory

- For reaction to occur
  → Particles must collide
  → must collide with $E \geq E_A$
  → must collide with appropriate geometry

Factors Affecting Rate of Reaction

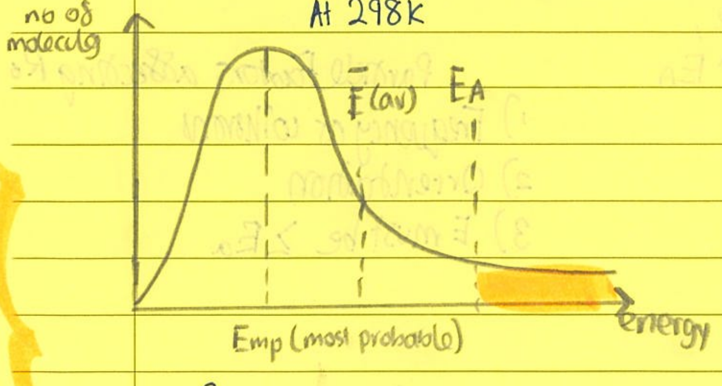
1) Temperature
2) Pressure
3) Concentration
4) Catalyst Usage
5) Surface Area

Maxwell-Boltzmann Distribution (MBDs)

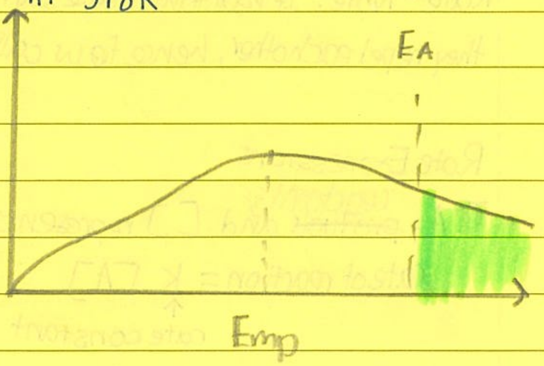
→ representation of distribution of energy amongst reactant particles

→ Area under graph ($\int y\,dx$) = total number of particles [never changes]

At 298K



At 398K



$\int y\,dx$ is the same for both but Emp is higher at 398 and more particles have $E \geq E_A$

All MBDs have horizontal asymptote = 0

All have no particles at 0 energy hence moves through origin

No of particles at Emp (298 K) lower to accomodate more particles at $E \geq E_A$

Explainadron Method → more collisions → more successful collisions → ↑ RofR

Collisions Per Unit Time!

2

Temperature

- ↑T, ↑ RofR (↑ $\frac{dy}{dx}$), reaches end faster
- More important reason → ↑ KE of particles, more successful collisions, ↑ RofR [more particles with $E \geq E_A$]
- Other → ma particles move faster → more collisions, more successful collisions, ↑ RofR

Surface Area Nve

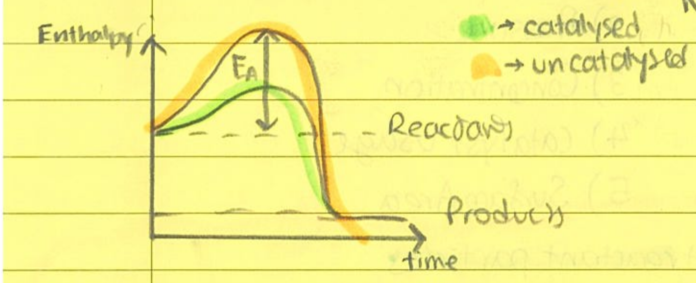
- More S.A, more particles that can come into contact with surrounding reagctant
- more collisions → more successful collisions → ↑ RofR

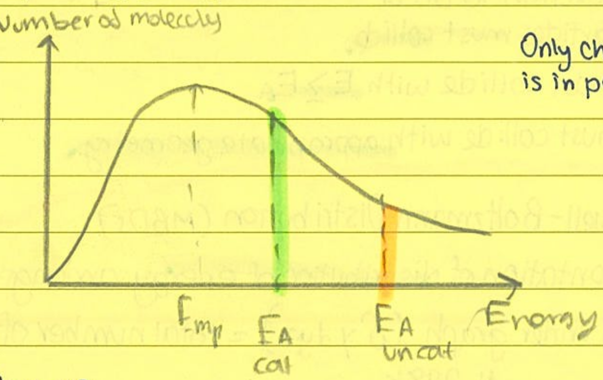
Pressure / Concendration

- ↑ conc/pressure, more collisions per unit time, per unit vol
- more successful collisions, ↑ RofR
- However RofR gets slower as reaction proceeds as ↓ conc of reactants, hence ↓ collisions

Catalysts

- → substances that ↑ RofR while without being chemically changed
- → bring reactant molecules closer togethor, hence reducing E_A, by providing alternative reaction pathway
- → More particles with $E > E_A$ ∴ ↑ rate because ↑ successful collisions





Only change in MBD is in position of E_A

~~Rate~~ Note: If reactant have same charge, they repel eachother, hence few collisions, ↑ E_A

Particle Factors affecting RoR
1) Frequency of collisions
2) Orientation
3) E must be $\geq E_a$

Rate Expressions

If A = ~~products~~ reactants and [ ] represents conc

rate of reaction = $K[A]$ ← K: rate constant

If you double the [A], and the rate doubles → $R = K[A]$

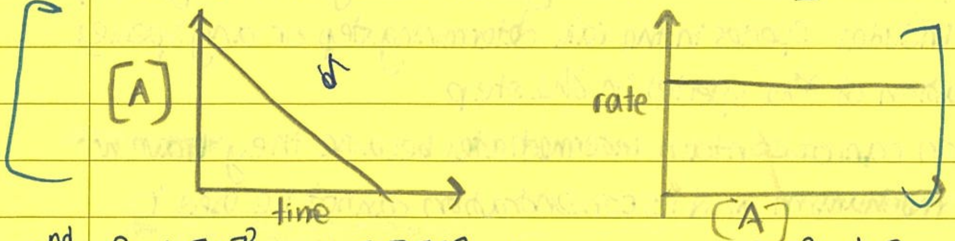
If you double the [A], and rate × 4 → $R = K[A]^2$

You can have [B] influencing reaction as well.

If no change in R when $\boxed{A}$ is doubled, $R = K[A]^0 = \underline{R = K}$

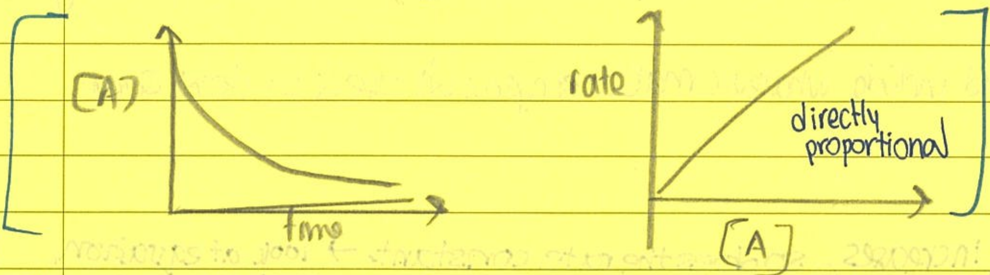
Orders [= sum of exponents]

1st → $R = k[A]$ where $k = s^{-1}$ [sum of exponents = 1]



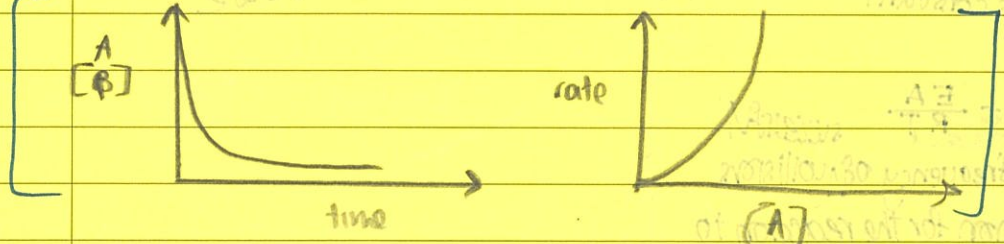
→ graphs here pertain to order 0

2nd → $R = k[A]^2$ or $k[A][B]$, where $k =$ ~~$mol\,dm^{-3}$~~ $dm^3\,mol^{-1}\,s^{-1}$



→ 1st Order Graphs

3rd → $R = k[A]^2[B]$ or $k[B]^2[A]$ or $k[B][A][C]$, where $k = dm^6\,mol^{-2}\,s^{-1}$



→ 2nd Order graphs

Reaction Mechanisms (construct of how overall reaction occurs)

→ comprise of all the elementary steps that ~~lead to the~~ occur in the reaction

→ Elementary steps outline overall reaction mechanism

Molecularity

- Number of ~~species (inclusive of ions molecules)~~ reactant particles involved in that step uni, bi and termolecular process.
- Uni → 1 reactant, Bi, 2 x, Ter, 3.
- Termolecular reactions are rare and unlikely because ~~of~~ 3 molecules are needed to collide with sufficient energy and correct orientation, very unlikely for this to occur. [statistically unlikely]

Note: Rate equations can only be determined experimentally

Intermediate - substance produced and consumed during elementary steps

e.g ~~N~~ $2NO_2(g) \rightarrow 2N_2(g) + O_2(g)$ [Overall]

$N_2O \rightarrow N_2(g) + O(g)$
$N_2O + O(g) \rightarrow N_2(g) + O_2(g)$ } elementary

O is an intermediate, as it is produced and consumed.

Determining the expression → by number of molecules involved in the step → coefficient

State what are the reactants in rate determining step.

Say if overall equation matches stoichiometric too. Rate of slow step with respect to intermediates, then replace

The rate determining step is the slowest elementary step (usually has v. high Ea)
∴ the rate expression includes species in the rate determining step or any species that lead to the formation of the species in the step

Note: Rate expression cannot contain intermediates because they have no role in overall reaction mechanism and its concentration cannot be used to assess change in rate because it is produced and consumed in elementary steps

Rate expression would include whatever makes compounds used in slow step

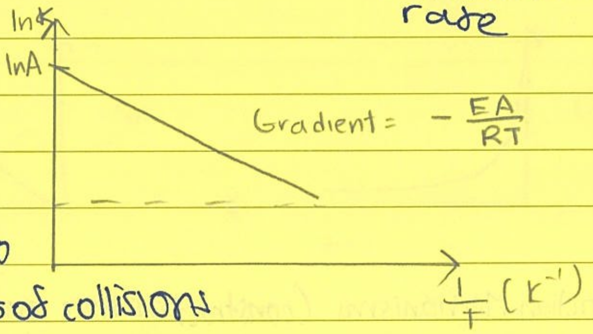
Arhenius

As the temperature increases, so does the rate constant. → look at equation, explain how k must increase to increase rate

$$\underset{\text{rate constant}}{\rightarrow} k = \underset{\uparrow \text{ Arhenius constant}}{A} e^{-\frac{E_A}{RT}} \quad \leftarrow \text{activation energy} \quad \leftarrow \text{8.31 and Temp}$$

$$\ln k = \ln A - \frac{E_A}{RT}$$

A also represents the frequency of successful collisions with correct orientation for the reaction to occur and relates to energy requirements of collisions



$$\boxed{\begin{array}{l}\ln A = y \text{ intercept} \\ -\frac{E_A}{RT} = \text{gradient}\end{array}}$$

Dependence of temperature

- If Ea low, then ↑ temp would have a small increase on k as less small increase in particles with $E \geq E_a$, small change in rate
- If Ea is high, ↑ temp, big ↑ k because large increase in particles with $E \geq E_a$, hence large change in rate

Simultaneous Arrhenius

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{-E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Ea is in $J mol^{-1}$

Ardon Pillay

Date No.

Chapter 7: Equilibrium

How to reach equilibrium

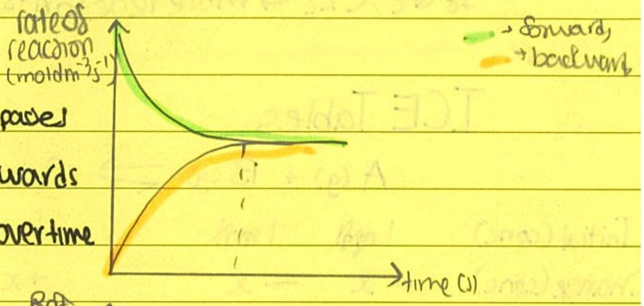
1) Closed system - if open → matter exchanged with surroundings, some of the products/reactants could escape hence cannot react, hence no equilibrium
2) No observable change in concentration of products or reactants
3) Rate of forwards reaction = rate of backwards reaction

Dynamic Equilibrium: A point at which the rates of the forwards and backwards reactions are equal and there is no observable change in the concentration of the reactants or products

Dynamic: because forwards and backwards reactions actively occur

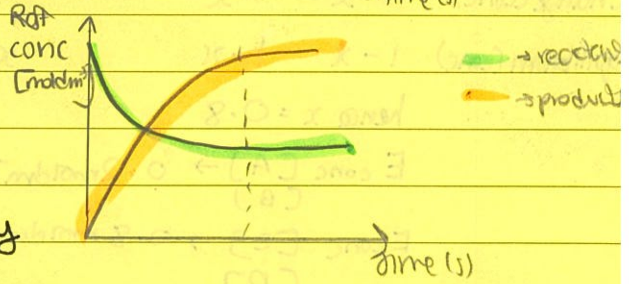
At equilibrium, there is no change in macroscopic properties, as these properties vary with reactant and product concentration and they do not change at equilibrium.

Microscopic Level [Rate]



- forwards reaction starts fast but rate decreases over time, due to less reactants being available as time passes
- Backwards starts at 0 as the products of the forwards have not been made yet, more of them available over time, hence rate increases
- When R of forwards and backwards are equal, the equilibrium reached

[Concentration]



- Conc of reactants decreases over time because they are being used in forwards
- Rate of decrease gets lower because ~~more~~ lower rate
- When conc of either reactants or products stay constant, the rates must be equal

Equilibrium Constant [Kc] and Reaction Quotient

~~If $K_c < 1$, forwards ~~reactants~~ favoured ~~(backwards)~~~~

~~If $K_c = 1$, same number of reactants as products~~

~~If $K_c > 1$, backwards ~~forwards~~ reaction favoured~~

Kc (constant)

- fixed value for a reaction for a certain temp [T]
- Not influenced by initial concentration
- increases over time as ↑ [products] and ↓ [reactants]

$K_c > 1$, products more than reactants

$K_c = 1$: same-same

$K_c < 1$, reactants more than products

$$A^x + B^y \rightleftharpoons C^2 + D^a$$

$$K_c = \frac{[C]^2[D]^a}{[A]^x[B]^y}$$ → but conc must be at equilibrium

FALCON

K_c trends → reciprocal of K_c is K_c for backwards reaction

- If the forwards reaction is endothermic, K_c increases as temperature does
- If it is exo, K_c decreases as temperature ~~does~~ increases

Reaction Quotient

- A measure of the relative amounts of products and reactants present during a reaction at a particular point

NOTE: For homogenous reactions (all prods + reactants same state), include everything in the rate expression. For hetrogenous (varied states), only include gases

If $Q_c > K_c$ → more products, hence backwards favoured

If $Q_c < K_c$ → more reactants, hence forwards favoured

ICE Tables

$A(g) + B(g) \rightleftharpoons C(g) + D(g)$

	A	B	C	D
Initial (conc)	1 ~~mol~~	1 ~~mol~~	1	1
Change (conc)	$-x$	$-x$	$+x$	$+x$
Equilibrium (conc)	$1-x$	$1-x$	x	x

information
- at equilibrium there are $0.2\,mol\,dm^{-3}$ of A

$1 - 0.2 = 0.8$

hence $x = 0.8$

E conc [A] [B] → $0.2\,mol\,dm^{-3}$

E conc [C] [D] → $0.8\,mol\,dm^{-3}$

$$\therefore K_c = \frac{[0.8][0.8]}{[0.2][0.2]} = \frac{0.064}{0.04}$$

$$K_c = \underline{\underline{16}}$$

K_c tips
1) If multiple elementary steps, multiply all their K_cs together to find K_c for the overall reaction
2) Reciprocal of K_c is the K_c of reverse reaction

Factors affecting Equilibrium

1) Concentration

$A + B \rightleftharpoons C + D$

$$K_c = \frac{[C][D]}{[A][B]}$$

- If [A]↑, the reaction counteracts the change by favouring the products, using up the added concentration and creating more products
- If [A]↓ the reaction counteracts the change by favouring the reactants, ~~&~~ making more A to ~~replinis~~ replenish what had been lost

OR

- Look at K_c, is [A]↑, K_c↓, and the lower it is, the more the forwards reaction is favoured
- If [C]↑, K_c↑, the higher it, the more the backwards reaction is favoured

Le Chatlier's Principle: If a dynamic equilibrium is disturbed by a change in conditions the reaction responds to counteract the change

Date No.

2) Temperature

$A + B \rightleftharpoons C + D \overset{\text{sit 1}}{[\Delta H -]}\overset{\text{sit 2}}{[\Delta H +]}\ \overset{\text{sit3}}{[\Delta H = 0]}$

- In Situation 1, increasing the temperature favours the backwards reaction as that reaction is endothermic and absorbs the added heat, counteracting the change in temperature
- In situation 2, increasing the temperature favours the forwards reaction as it is endothermic and absorbs the heat added, counteracting the change
- In sit 3, change in temperature does not affect equilibrium

3) Pressure

$A + B \rightleftharpoons 2C + 3D$

- Increasing pressure shifts the equilibrium ~~with the~~ to the side that has the least gas molecules [favouring the reaction that produces it] because with fewer gas molecules, less force is applied on nearby surfaces, counteracting the change by reducing pressure
- If both sides have the same number of gas molecules, then changes in pressure do not affect the position of equilibrium

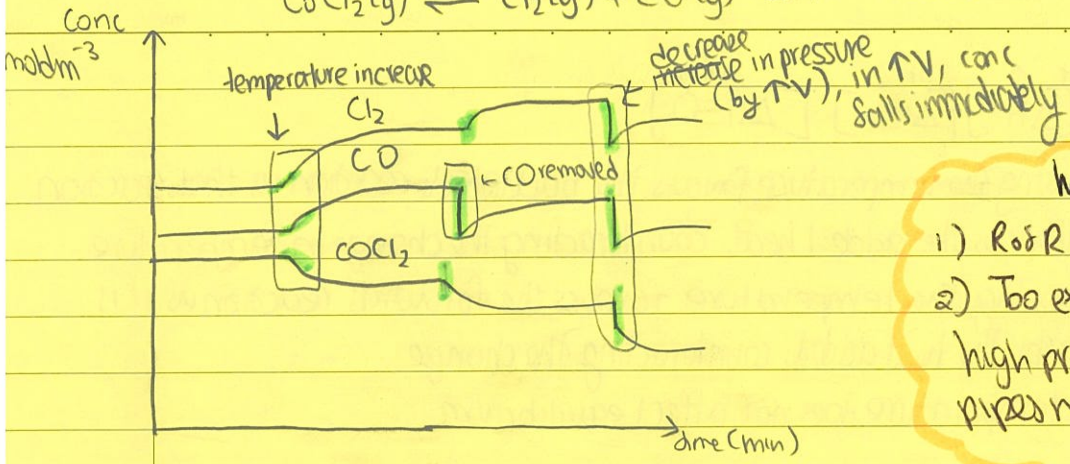
Terms to know and things about them

1) % yield - $\frac{\text{real}}{\text{theoretical}}$ → if this needs to be increased, exclude ~~pre~~ concentration
2) Shift to right / left → whatever is on that side is produced to a greater extent
3) ↑ Volume → ↓ pressure, viceversa

NOTE: A catalyst only decreases Ea, it does not affect equilibrium or K_c but speeds up the forwards + backwards reactions to equal extents

Condition Change	System Change	Explanation
↑ P	↓ P	equilibrium shifts to side with least gas molecules, reducing pressure by reducing the numb of particles colliding with surfaces
↑ T	↓ T	equilibrium shifts to products of endothermic as endothermic takes in heat released
↑ [A]	↓ [A]	Reaction uses up added A and hence produces more of the other side, shifting equilibrium there

$CoCl_2(g) \rightleftharpoons Cl_2(g) + CO(g)$ $\Delta H = +108kJ$



Why don't we use optimal conditions?

1) RofR too low (e.g Haber)
2) Too expensive to create desired high pressure, expensive reinforced pipes needed

Note that when $K_c \leftrightarrow 0$, [reactant]$_{initial}$ is the same as [reactant] equilibrium

ΔG and Equilibrium

Recap

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G_{prod} - G_{reactants}$

convert to $0.00831\ kJmol^{-1}K^{-1}$

$$\Delta G = -RT\ln K_c$$

If ΔG of forward reaction is −ve, forward reaction favoured as reverse must be +ve. Equilibrium is when ΔG is minimised and ΔS is maximised, hence when ΔG = 0

Summary of relationships

ΔG	K_c	ln K	Mixture
−ve	$K_c > 1$	ln k = +ve	more products
+ve	$K_c < 1$	ln k = −ve	more reactants
0	$K_c = 1$	ln k = 0	Equal quantities

Kinetics and Equilibrium

for $A + B \rightleftharpoons C + D$

Rate (forward) = $k[A][B]$
Rate (backwards) = $k'[C][D]$
} assuming overall Order = 2

at equil

$$k[A][B] = k'[C][D]$$

$$\frac{k}{k'} = \frac{[C][D]}{[A][B]} = K_c$$

$\frac{K}{K'} = K_c$ → This explains why a catalyst does not affect K_c, as k and k' are multiplied by the same factor that is canceled out ($K_c = \frac{k(x)}{k'(x)}$)

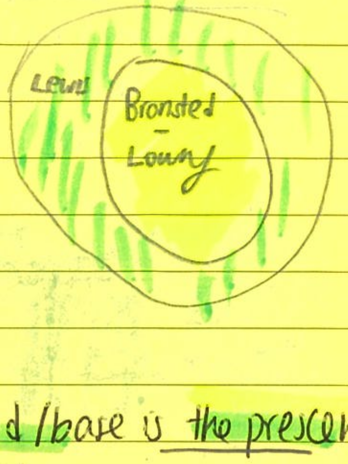
↘ Furthermore, conc does not affect K_c as it does not affect k or k'.

↓ Additionally, temperature affects K_c because of $k = FAe^{-\frac{EA}{RT}}$. hence each k increases with T, but each constant is affected differentally than the other. For an endo, K_c ↑ because Ea (forwards) > Ea (backwards), ∴ k [illegible] ~~leading to~~ increases faster than k' → ↑ K_c

Date No.

8: Acids and Bases

~~8.11~~



Definitions of Acids and Base

Bronsted Lowry acid - Proton Donor [H^+]

Bronsted Lowry base - Proton Acceptor [H^+]

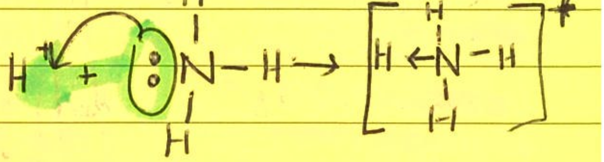
e.g.

$$\underbrace{HCl(g)}_{acid} + \underbrace{H_2O(l)}_{base} \rightleftharpoons \underbrace{H_3O^+(aq)}_{c.\ acid} + \underbrace{Cl^-(aq)}_{c.\ base}$$

The difference between a conjugate base / acid and acid / base is the presence of a H^+ ion.

(electrophile)
Lewis Acid: A lone electron pair acceptor

Lewis Base: A lone electron pair donor
(nucleophile)



Lewis theory

- includes BL acids and alkali but includes those that has a full valence shell, the H^+ can be replaced with an atom with an empty ~~change~~ orbital
- Always involves formation of dative bond,
- See the NH_3 reaction

An amphiprotic (→ gain or lose protons) substance is one that can acts as a Lowry ~~Lewis~~ Acid or Base.
E.g H_2O - Oxygen has 2 lone pairs [can function as a lewis base] and has 2 hydrogen atoms attached that can be lost as H^+ ions, hence H_2O would act as a proton donor.

Reactions

1) Acid + Carbonate → Salt ~~(carbonate)~~ + Water + carbon dioxide
2) ~~Acid + ammonia base → ammonia gas + salt~~
3) Acid + Base → salt + Water [but e.g of exception → $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$]
4) Acid + Metal (reactive) → salt + hydrogen gas
5) Acid + metal oxide → salt + water [$-\Delta H$]
6) Acid + hydrogencarbonate → salt + water + CO_2

fully dissociates
weak conjugate base
strong conjugate base

Strong vs Weak Acid / base

partially dissociates

- Determined by the extent to which they ionise in solution
- We can determine this by ~~determining~~ observing the equilibrium of the reaction, if it lies to the reactants – the acid / base has not fully ionised → ergo it is a weak acid / base
- There are certain acids and bases whose reactions go to completion

Strong Acids [weak c. base]	Strong bases [weak c. acid]
○ HCl	○ LiOH
○ HNO_3	○ NaOH
○ H_2SO_4 [only first ionisation]	○ KOH and $Ba(OH)_2$
Weak Acids [strong c. base]	**Weak Bases [strong c. acid]**
○ H_3PO_4	○ NH_3
○ CH_3COOH or any organics	○ ethyamine or any amines
○ H_2CO_3	

○ weak conjugate acid/bases are v. stable, hence equil ~~so~~ favours r.h.s

Experimental Methods

[based on principle that greater strength = higher concentration]

1) Electrical Conductivity
- higher concentration of mobile ions begets a larger number of charged particles available to carry a charge throughout a solution [for strong base/acids]
- Use electrodes + ammeter ↳ ∴ greater electrical conductivity
- if asked, ~~say~~ test conductivity and that one is a better conductor than the other

2) Rate of Reaction
- ↑ $[H^+]$ / $[OH^-]$, more collision per unit time per unit volume, increasing the rate → this matches that of a strong acid / base (as ↑ $[H^+]/[OH^-]$)
- use a reaction with a strong metal or acid / alkali, say the reaction is more vigorous

3) pH
→ $-\log_{10}[H^+]$: conc of H^+ ions in mol/dm³
→ The lower this number, the more acidic something is
→ direct measurement of $[H^+]$ → defines strength

X - Protic Acids

- X → number of protons that can be lost
- ionises in X steps and % ionisation decreases with each step because negative charge builds on the conjugate base, more energy needed to remove a H^+ from it, equil shifts to ~~right~~ left

because strong acid

e.g $H_2SO_4(l) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$

Roxanne

2

pH calculations

pH (potential hydrogen) = $-\log_{10}[H^+]$ and $[H^+] = 10^{-pH}$ Date No.

Example Question

(1) 10ml of H_2SO_4 [0.1 mol/dm^3] was added to 5ml of 0.1 mol/dm^3 NaOH. What is the pH of the final solution

① Write the equation

$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$

② Determine the limiting reagent

Moles of H_2SO_4 available = $\frac{10}{1000} \cdot 0.1 = 0.001$

Moles of NaOH available = $\frac{5}{1000} \cdot 0.1 = 0.0005$ → ∴ this is the limiting reagent as 0.00025 moles of H_2SO_4 need react with it

③ Find the moles of the excess solution left

$\frac{0.0005}{2} = 0.00025$ [moles of H_2SO_4 needed]

$0.001 - 0.00025 = 0.00075$ moles

④ Depending on the protic nature of the solution, find the moles of H^+

As this is H_2SO_4, $0.00075 \times 2 = 0.0015$ mole

⑤ ÷ this by total volume of solutions [VIP]

$\frac{0.0015 \text{ moles}}{0.015 \text{ dm}^3} = 0.1 \text{ mol dm}^{-3}$

⑥ Apply pH equation

$-\log_{10}[0.1] = 1$

$-\log_{10}OH$ $-\log_{10}(k_w)$

pOH, k_w, pkw, kb, pkb a, ka, pka   that's a lot to know!

pOH = $-\log_{10}[OH^-]$ OR $2H_2O \rightleftharpoons H_3O^+ + OH^-$

$k_w = k_c[55 \text{ moldm}^{-3}] \longrightarrow H_2O \rightleftharpoons H^+ + OH^-$

$k_w = 1 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$ at 298k $\therefore k_c = \frac{[H^+][OH^-]}{[H_2O]^2}$

$k_w \uparrow$, $T \uparrow$ because as $\uparrow T$, $\uparrow k_c$

As $T\uparrow$, $\uparrow [H^+]$ and $[OH^-]$, hence $\downarrow$ pH and $\downarrow$ pOH $[H_2O]$ is constant, at 55

∴ k_w (ionic product of water)

$-[\log_{10}[H^+] + \log_{10}[OH^-]] = 14$ at 298k   ↓ $k_w = [H^+][OH^-]$

OR

pH + pOH = pkw

pkw = $-\log_{10}[k_w]$

$+\sqrt{k}$ = $[H^+]$ or $[OH^-]$

FALCON

Karma Chameleon

A note on pH and neutrality.

Note the equation $2H_2O \rightleftharpoons H_3O^+ + OH^-$

The $[OH^-]_{aq} : [H^+]$ is 1 : 1.

Even though pH would change with T, the $OH^- : H^+$ stays at 1:1, this makes a solution neutral.

FOR NEUTRALITY → $[H^+] = [OH^-]$

FOR ACIDITY → $[H^+] > [OH^-]$

FOR BASIC NATURE → $[H^+] < [OH^-]$

↗ [SEE FINAL PAGE]

K_a (acid disassociation constant) → Expression of the strength of weak acid / base

→ used for weak acids

For the equation ~~$HA \rightleftharpoons A^- + H^+$~~ 1) $H_2O + HA \rightleftharpoons H_3O^+ + A^-$

$$k_c = \frac{[H_3O][A^-]}{[HA][H_2O]}$$

but, we assume $[H_2O]$ is constant ~~so~~ at 55M

$$k_c[H_2O] = \boxed{\frac{[H_3O^+][A^-]}{[HA]}} = K_a$$

$pka = -\log_{10}(ka)$

$pK_b = -\log_{10}(K_b)$

another assumption we make is that $[HA]$ does not change, as we know that this is a weak acid

K_b is identical (-ish)

For 2) $B + H_2O \rightleftharpoons BH^+ + OH^-$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

the same story unfolds.

Note: if we flip 1 or 2 around

1′ → $A^- + H_3O^+ \rightleftharpoons H_2O + HA$ → base [base is A^-]

2′ → $BH^+ + OH^- \rightleftharpoons B + H_2O$ → acid [acid is OH^-]

So, their K_as/K_bs become K_b/K_a, with the reciprocal of the old one.

E.g 1′ → $K_b = \frac{[HA]}{[H_3O^+][A^-]}$

Example: The pH of a 0.020 mol dm^{-3} solution of weak monoprotonic acid is 3.9. Find Ka.

Step 1: Write equation for ka → $\frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[0.02]} = ka$

$ka = (10^{-3.9})^2$

Buffer solutions

- Definition: a solution that resists changes in pH when small amounts of acids or alkali are added
- Consists of a ~~strong~~ weak acid/base with its stronger conjugate base

2 Ways of formation

1) weak acid/base + salt containing conjugate acid/base

e.g $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$] in solution together
$NaCH_3COO(sl) \longrightarrow Na^+ + CH_3COO^-$]

√.

2) weak acid/base + ~~aci~~ strong acid/base holding conjugate base/acid in limited quantities ← because we need acid leftover for buffer

→ will form strong salt containing the conjugate base/acid that can be disassociated

e.g $CH_3COOH + NaOH \rightarrow NaCH_3COO + H_2O$ [with excess CH_3COOH)

$A = CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ [system with diss acid + conjugate
$B = NaCH_3COO \rightarrow Na^+ + CH_3COO^-$] base

Resisting Changes [Acidic Buffers]

Consider the system above

1) addition of H^+ ions → equilibrium of A shifts to the left, using up the added H^+ to produce additional CH_3COOH, hence $[H^+]$ does not change [for calc] reacts with CH_3COO^- to prod CH_3COOH
2) Addition of OH^- → reacts with CH_3COOH to produce H_2O and CH_3COO^-, no change in $[H^+]$, by consuming added OH^-

Resisting Change [Basic Buffers]

e.g ~~NH_3~~ $NH_4Cl \rightarrow NH_4^+ + Cl^-$
$NH_3 + H_2O \rightleftharpoons OH^- + NH_4^+$

1) Addition of H^+ → ~~react with OH^- to form H_2O, ensure $[H^+]$ stays constant~~ reacts with NH_3 to form ~~a~~ NH_4^+, $[H^+]$ doesn't change
2) Addition of OH^- → ~~shifts equil to left in order to consume added OH^-, $[H^+]$ stays constant~~ reacts with the ~~H^+~~ NH_4^+ to produce NH_3 and H_2O → $[H^+]$ constant

Why do we add more of the conjugate?

- we need high conc as the conjugate base/acid is used in maintaining pH,
- weak base/acid only weakly, not enough of conjugate
- Hence ionic salt holding it added so it fully dissassociates, allowing for sufficient quantities

Factors Affecting Buffers

- Dilution: ↑ dilution, ↓ buffering capacity: amount of acid/base that can be absorbed without change in pH, this decreases as the molar conc of buffering components ↓
- Temp: affects K_a and K_b, hence affects pH. VTP to have constant temp in blood transfusions – due to blood buffers

Why don't we use strong bases?

Date No.

e.g $HCl \rightarrow Cl^- + H^+$

No equilibrium to be shifted when H^+ added, hence $[H^+]\uparrow$, $\downarrow pH$

Addition of OH^- consumes H^+, hence $[H^+]\downarrow$, $\uparrow pH$

Henderson-Hasselbalch Equation

$pH = pka - \log_{10}\left[\frac{[acid]}{[salt]}\right]$

$pOH = pk_b - \log_{10}\left(\frac{[base]}{[salt]}\right)$

Assumptions

1) $[acid/base]_{initial} = [acid/base]_{final}$ - assumes v. weak dissassociation

2) salt fully dissassociates

if $[salt] = [acid]$,

$pH = pka$

$pOH = pkb$

because $pka - \log_{10}[1]$

$= pka - 0$

Example

A buffer has 0.1 mol of CH_3COOH and 0.13 mol of $NaCH_3COO$ in $1dm^3$ of solution.

(a) pH of buffer?

(b) pH when 0.02 mol of KOH added?

(c) pH when 0.02 mol of HNO_3 added?

Pre-requisites

1) If acid/alkali is used to form salt, must be l. reagent, otherwise no weak acid or base left → cannot resist change in pH

2) Conjugate needed → to react with OH^- / H^+ → ∴ we add salt

(a) $pH = pka - \log_{10}\left(\frac{0.10}{0.13}\right)$

$pH = 4.76 - \log_{10}\left(\frac{0.10}{0.13}\right)$

$pH = 4.87$

(b) $KOH + CH_3COOH \rightarrow K^+ + CH_3COO^- + H_2O$

	KOH	CH_3COOH	CH_3COO^-
I	0.02	0.10	0.13
E	0	0.08	0.15

← Note: consideration of c. base and acid

$\therefore pH = 4.76 - \log_{10}\left(\frac{0.08}{0.15}\right)$

$= 5.03$

(c) $H^+ + \cancel{NO_3^-} + CH_3COO^- \rightarrow CH_3COOH + \cancel{NO_3^-}$

	H^+	NO_3^-	CH_3COO^-	CH_3COOH
I	0.02	0.02	0.13	0.10
E	0		0.11	0.12

$pH = 4.76 - \log_{10}\left(\frac{0.12}{0.11}\right)$

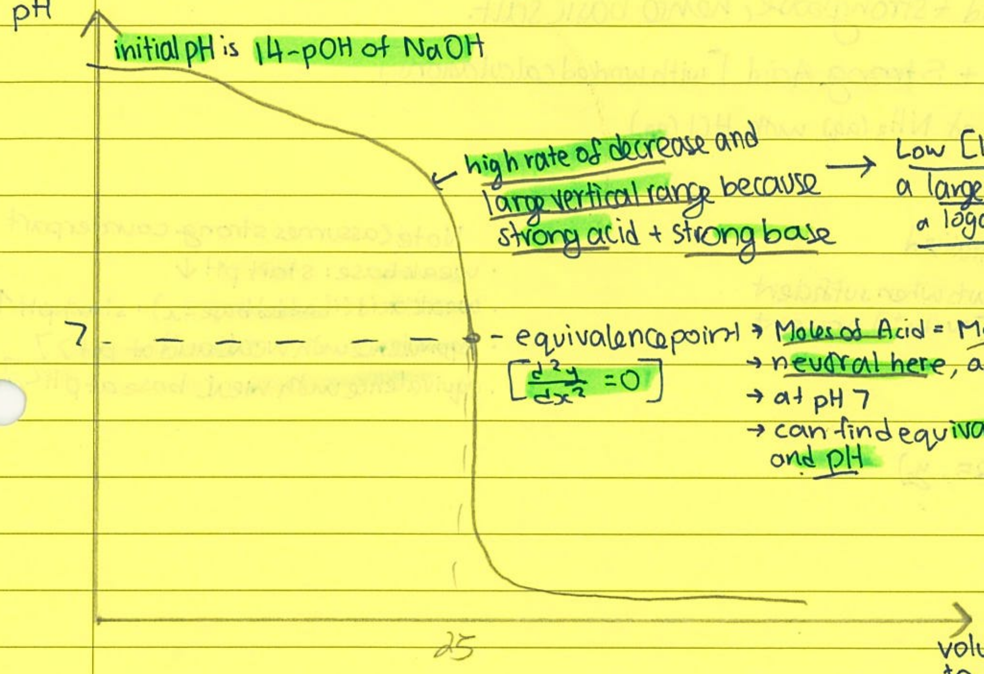
$= 4.72$

pH curves

- with pH on y and volume of acid/base added on the x axis

Shape 1 (strong Acid + Strong Base)

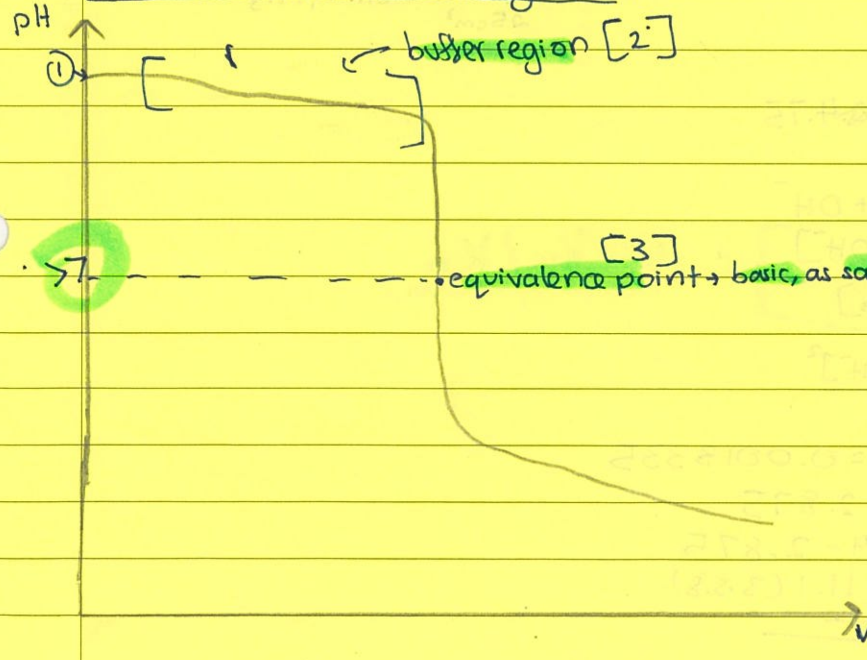
initial pH is 14-pOH of NaOH



← high rate of decrease and large vertical range because strong acid + strong base → Low [H⁺], ∴ small addition of [OH⁻] has a large effect on pH, given that pH is a logarithmic scale

- equivalence point $\left[\frac{d^2y}{dx^2}=0\right]$
  → Moles of Acid = Moles of Base
  → neutral here, as salt is neutral → strong acid + s. base
  → at pH 7
  → can find equivalence volume and pH

Shape 2 (weak acid + strong base)



← buffer region [2]

[3]
equivalence point → basic, as salt produced will be basic

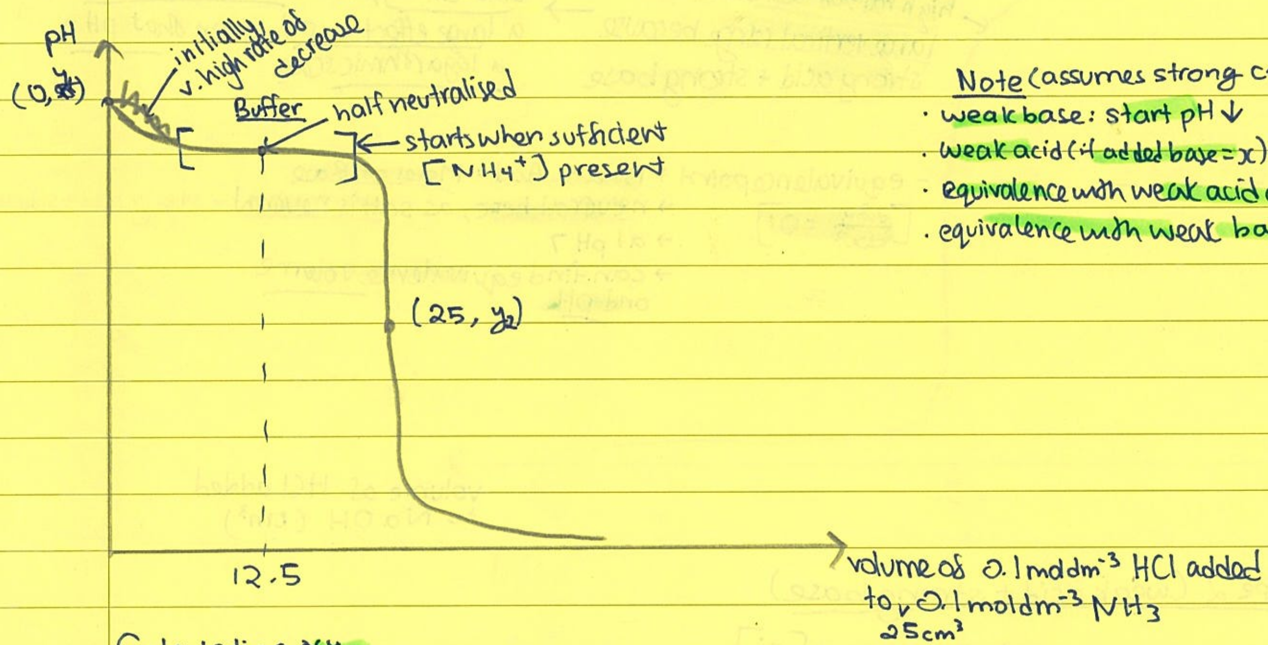
① Determined by strength of acid or base depending on x axis. Use either pka, pkb or full dissassociation to determine

② Buffer Region: Consider the salt of CH_3COOH + NaOH, $NaCH_3COO$. It dissassociates into Na^+ and CH_3COO^- (strong conjugate base). Once sufficient CH_3COONa is present ~~CH_3COO bonds forms a dative covalent bond with H^+ in solution, ↓ [H⁺]~~ ↑ If more H^+ is added, it simply reacts with ~~the added~~ added H^+ to produce CH_3COOH, consuming added H^+ and resisting

③ - Equivalence Point: ~~for~~ Still when moles of acid = moles of base. However, the salt produced here would be basic as $NaCH_3COO_{(s)} \rightarrow Na^+(aq) + CH_3COO^-(aq)$. The CH_3COO^- forms a dative covalent bond with a surrounding H^+, ↓ $[H^+]$ ∴ ↑ pH at equivalence. Say that salt was formed from weak acid + strong base, hence basic salt.

Shape 3: Weak base + Strong Acid [with worked calculations]

Consider the titration of $NH_3(aq)$ with $HCl(aq)$.



Note (assumes strong counterpart)

- weak base: start pH ↓
- weak acid (if added base = x): start pH ↑
- equivalence with weak acid at pH > 7
- equivalence with weak base at pH < 7

Calculating ~~x~~ y,

$V = 25cm^3$

$C = 0.1 mol/dm^3$

$pK_b = 4.75$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$\boxed{K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}} \leftarrow \text{Use } K_b / K_a$$

$$10^{-4.75} = \frac{[OH^-]^2}{0.1}$$

$$\therefore [OH^-] = 0.0013335$$

$$pOH = 2.875$$

$$pH = 14 - 2.875$$

$$y_1 = pH = 11.1 \ (3.s.8)$$

Buffer Region

Ionic salt produced by $NH_3 + HCl$ (NH_4Cl), dissassociates into NH_4^+ and Cl^-.

∴ we have a system in place, once enough NH_4^+ is produced, that can be a buffer

Thus, adding more HCl results in limited pH change as added H^+ is reacted with NH_3 to produce NH_4^+, consuming added ~~NH~~ H^+. This can be proven by the Henderson Hasselbach Equation

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Y_2

- Realistically, Y_2 should be < 7. This is because NH_4Cl is acidic in solution

Proof

$$NH_4Cl_{(aq)}^{(s)} \rightarrow NH_{4(aq)}^{+} Cl^{-}_{(aq)}$$

$$\underset{\boxed{\text{cation hydrolysis}}}{\overset{}{NH_4^+}} + H_2O \rightleftharpoons NH_3 + \underline{H_3O^+}$$

added H_3O^+, ∴ ↑ $[H^+]$ and ↓ pH

Half-Neutralisation

- for pH = pka or pOH = pkb, [base/acid] = [concentration of salt]. This can happen when half of the solution being titrated is neutralised, because

- Calculation

$$NH_3 + HCl \rightarrow NH_4Cl$$

	NH_3	HCl	NH_4Cl
Ini:	0.0025	0.00125	0
Cha:	−0.00125	−0.00125	+0.00125
End:	$\boxed{0.00125}$	0	$\boxed{0.00125}$

pH at this point = ~~pk~~ 14 − pkb

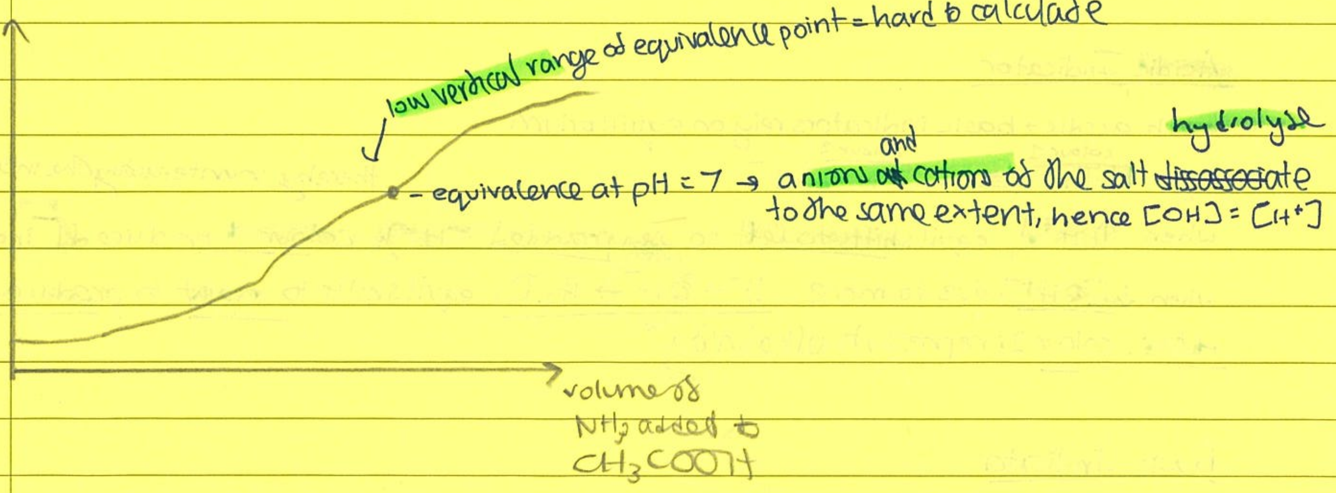
$$pOH = pkb - \log_{10}\left(\frac{[NH_3]}{[NH_4Cl]}\right)$$

$$= pkb$$

$$= 4.75$$

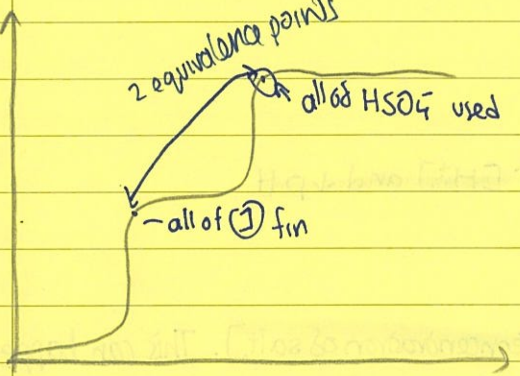
pH = ~~4~~ $\underline{\underline{9.25}}$ at $\underline{x = 12.5}$

Weak Acid + Weak Base [Curve 4]



Polyprotic Acids

$H_2SO_4 + NaOH \rightarrow$ $H_2SO_4 \cancel{\rightleftharpoons} \rightarrow H^+ + HSO_4$ ①



→ NOT ASSESSED!

Strong vs Weak [Acids]

lower equivalence	higher equivalence
lower start	higher start
high vertical range of equiv	low vertical range of equivalene

Salts [consider conjugates]

s.a + s.b → neutral salt + water
w.a + s.b → basic salt + water
s.a + w.b → acidic salt + water
w.a + w.b → neutral salt + water
cations and anions hydrolyse to same extent

Indicators

- Definition: An indicator is a weak acid or base that changes colour when it becomes dissassociated
- point at which it changes colour = end point
- Equivalence point must match end point, ∴ endpoint must be within vertical range of the equiv
- S Especially considered with weak acids / bases as their vertical range is smaller
- usually weak acids or bases

Acidic Indicator

- both acidic + basic indicators rely on equilibrium
- e.g $\overset{\text{colour 1}}{HInd} \rightleftharpoons \overset{\text{colour 2}}{H^+ + Ind^-}$, thereby counteracting the increase $[H^+]$

when $\uparrow[H^+]$, equil shifts to left to use up added $[H^+]$, colour 1 produced [indicates acidity
when $\downarrow[OH^+]$ due to more $H^+ + OH^- \rightarrow H_2O$, equil shifts to right to produce more H^+, ∴ colour 2: represents alkalinity

Basic Indicator

- e.g $\underset{\text{colour 1}}{BOH} \rightleftharpoons \underset{\text{colour 2}}{B^+} + OH^-$

when $\uparrow[H^+]$, more OH^- reacts with it, equil shifts to right, colour 2 expressed, thus is the acidic colour. When $[OH^-]\uparrow$, equil shifts to left, colour 1 expressed, ~~acidic~~ basic colour

NOTE

Always write indicators like this $HIn_{(aq)} \rightleftharpoons H^+_{(aq)} + In_{(aq)}$ //

$\boxed{\text{colour1}}$ $\boxed{\text{colour2}}$

Kind and PKind

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$K_{ind} = \frac{[Ind^-][H^+]}{[HInd]}$ → halfway through colour change $[Ind^-]$ or $[H^+] = [HInd]$

↳ ∴ mix of colour 1 and 2

∴ $K_{ind} = [H^+]$

and pKind would = pH. Only at the halfway point.

However, this does not always happen, so we do $\boxed{\pm 1}$, to produce a colour change interval. e.g for methyl orange → pKind = 3.7 but $3.1 < pH < 4.4$

Must select appropriate range that will be the same range of the equivalence point.

↳ phrase: "indicator end point within range of pH at equivalence."

Why is there a change in colour?

The energy gap of undissociated and dissociated will vary, hence as different degrees of π bond conjugation in each states. Hence different wavelengths of light absorbed and then transmitted.

Table of how different combos affect range of equivalence point

S.A + S.B	3 – 11, 7 in middle
~~S~~W.A + ~~W~~S.B	7 – 11, 9 in middle
~~S~~W.B + ~~W~~S.A	3 – 7, 5 in middle
W.A + W.B	No sig change of pH at equiv, but usually 7

$\boxed{\pm 2}$ for S.A or S.B

Acid Deposition

Why is rainwater acidic?

- Usually pH 5.65
- dissolved CO_2 which forms carbolic acid
- ∴ acidic rain = rain with pH < 5.60

$H_2O + CO_2 \rightleftharpoons H_2CO_3$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

✱ Acidic Deposition: Process by which acidic particles, gases and precipitates leave the atmosphere

Wet Acid Deposition

- fall to ground as aqeous precipitates (referring to the acidic material), e.g snow, rain, hail)

Dry Acid Deposition

- Acidifying particles, gases fall to ground as smoke / dust and later dissolve to form acids.

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Sulfur Oxides

- SO_2 from burning fossil fuels [coal + heavy oil] and smelting [iron from ore]

$S(s) + O_2(g) \rightarrow SO_2$ [$-\Delta H$]

$SO_2(g) + H_2O(l) \rightarrow H_2SO_{3(aq)}$ (sulfurous acid)

OR

$2SO_2 + O_2 \rightarrow 2SO_3$ [in sunlight]

$SO_3 + H_2O \rightarrow H_2SO_4$

~~dry acid deposition~~

hydroxyl radical in atmosphere [one unpaired e^-] → $\boxed{OH^{\bullet}} + SO_2 \rightarrow {}^{\bullet}\overset{HO}{\cancel{OH}}SO_2$

${}^{\bullet}\underset{+O_2}{HOSO_2} \rightarrow {}^{\bullet}HO_2 + SO_3$

} Photo oxidation

Nitrogen Oxides

- NO for instance is formed from the heat of internal combustion engines or from lightning strikes

$N_2 + O_2 \rightarrow 2NO \rightarrow -\Delta H$, v. high energy needed

$2NO + O_2 \rightarrow 2NO_2$

Acidification

$2NO_2 + H_2O \rightarrow \underset{\text{nitrous acid}}{HNO_2} + HNO_3$ ← nitric acid

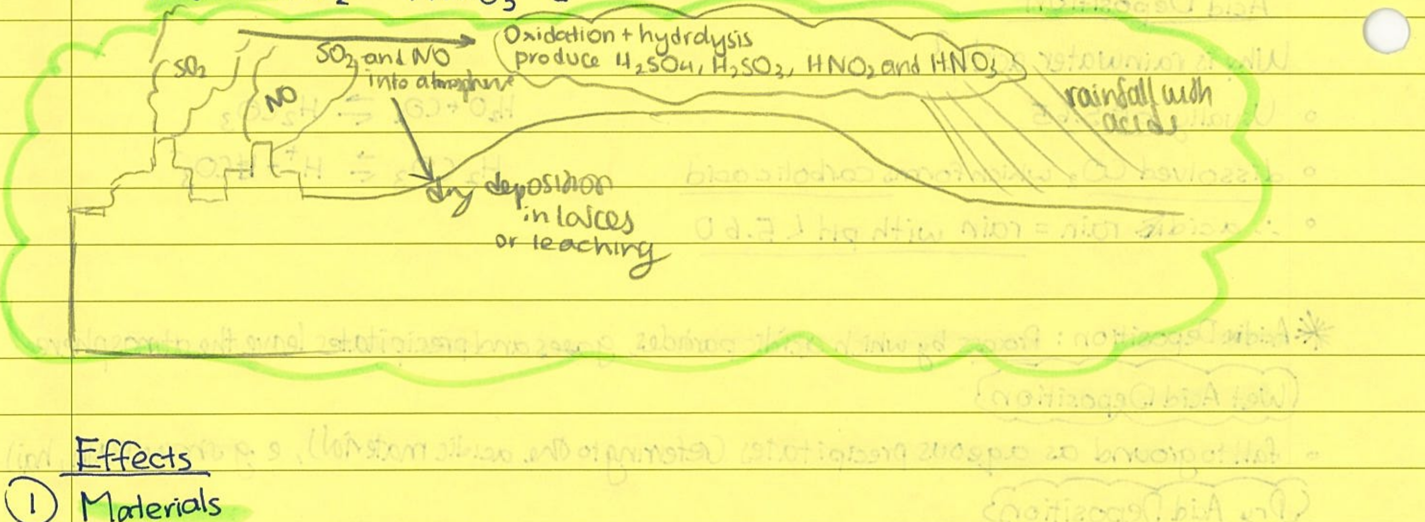
OR

~~$2NO_2 + 4H_2O + O_2 \rightarrow 4HNO_3$~~ ~~2N~~ $4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$

$H^{\bullet}O + NO \rightarrow HNO_2$

$H^{\bullet}O + NO_2 \rightarrow HNO_3$

} Photo oxidative reaction



Effects

① Materials

- marble and limestone made of $CaCO_3$
- react with H_2SO_4, ~~H_2SO_3~~ and SO_2 (dry deposition) to form $CaSO_4$

$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$

$2CaCO_3 + 2SO_2 + O_2 \rightarrow 2CaSO_4 + 2CO_2$

- Also reacts with nitric acid → $2HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$
- $CaSO_4$ ~~and $Ca(NO_3)_2$~~ very soluble, hence washes off the limestone easily
- $CaSO_4$ and $Ca(NO_3)_2$ bigger than $CaSO_3$ in Mr, hence creation causes expansion and cracking

Metals

- dry deposition and wet react with metals, e.g Iron
- $Fe(s) + SO_2 + O_2 \rightarrow FeSO_4$
  $Fe + H_2SO_4 \rightarrow H_2(g) + FeSO_4$ → enables ionic conductivity ↓ increase in rate of electrochemical corrosion reactions
- Acid rain can remove protective oxide coatings
  eg $Al_2O_3 + 6H_2SO_4 \rightarrow 2Al_2(SO_4)_3 + 3H_2O$ (Al oxide plus H_2 ... → Al (acid r.b))
  ∴ causes damage to bridges, roads + tracks.

Lakes + Water Bodies

- ~~Causes leaching of importan'~~
- Reacts with $Al(OH)_3$ in rock to form soluble, toxic Al^{3+}
  $Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$
- Al^{3+} interferes with gill operation → cannot take in O_2
- Cause eutrophication due to nitrates in acid rain → algal blooms ~~redu~~ increases BCO demand, death of ecosystem.

Plants

- Al^{3+}, in the same reaction, damages roots, cannot take in nutrients → stunted growth and yellowing + loss of leaves, thinning of tree tops
- Acid Rain causes leaching of nutrients like Ca^{2+} and Mg^{2+} → needed for chlorophyll, cannot photosynthesise
- dry deposition block stomata – no gas exchange

Humans

- Fine sulfate and nitrate particles irritate mucous membranes → ↑ risk of asthma, bronchitis and emphysema.
- Heavy metal ions like Al^{3+} in water could cause Alzheimers.

Salts [overall pH determined by the comparative hydrolysis of cations and anions]

Cation Hydrolysis

~~$H^+ + H_2O \rightleftharpoons OH^- +$~~

$\cancel{A^+} B^+ + H_2O \rightleftharpoons BOH + \boxed{H^+}$

↓ comes about from a salt created by a weak base but strong acid

↑ increased $[H^+]$, ∴ acidic

e.g

$NH_4^+ + H_2O \rightleftharpoons NH_3 + \boxed{H_3}O^+$

↑ $\boxed{H^+}$

Anion Hydrolysis

$\boxed{A^-} + H_2O \rightleftharpoons HA + \boxed{OH^-} \rightarrow \uparrow [OH^-]$, ↓ pH ∴ basic

↑ from salt by reaction between strong base weak acid

e.g → $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \boxed{OH^-}$

If cations and anions hydrolyse to same extent, pH = 7.

* Note: Group 1 + 2 cations cannot hydrolyse to form H^+ as their charge densities are too low

Metal Cation Hydrolysis

Consider $[Al(H_2O)_6]^{3+}$

- Al^{3+} is a metal cation with a high charge density
- This high charge density allows it to polarise the O−H bond in water, weakening it in the process
- Therefore, it allows for a H^+ ion to leave a H_2O and react with another H_2O to form the hydroxonium ion

$$[Al(H_2O)_6]^{3+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_5OH]^{2+}_{(aq)} + \boxed{H_3O^+}$$

This keeps happening [~~addition of OH⁻~~ and loss of H^+] until the complex ion loses it's charge, thus it can no longer dissolve $[[Al(H_2O)_3(OH)_3]_{(s)}]$. Forms a precipitate

∴ Metal Cations form acidic solution by ↑ $[H^+]$

NOTE: If you have XA, where X is a transition metal iron and A^- is a anion, you must use the hydrated complex ion of X and explain from there.

X^{2+} for example → $[X(H_2O)_6]^{2+}$

↑ brackets: charge distributed across molecule

Post Combustion Methods of reducing SO_2 and NO_x emissions

1) Flue Gas Desulfurisation

- $Ca(OH)_2(s) + SO_2(g) \rightarrow CaSO_3(s) + H_2O$
  [calcium sulfite]

- $2CaSO_3(s) + O_2(g) + 4H_2O(l) \rightarrow \boxed{2CaSO_4 . 2H_2O(s)}$
  (gypsum)

- gypsum or hydrated calcium sulfate can be used to make plaster and cement

2) Catalytic Converter

- honey-comb interior to increase S.A for contact with gases
- Uses porous Al_2O_3 as coating with platinum and other precious metals.
- Catalyses the reduction of NO_xs into N_2 and O_2
  e.g $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$

3) Lower Temperature Combustion

Δ1 ∴ shift to left, when ↑T

$\underline{N_2 + O_2 \rightleftharpoons 2NO}$ $[+\Delta H]$

- formation of NO reduced at lower temperatures
- can be accomplished by recirculating exhaust gases into the engine. ↓NO in emission

Pre Combustion

1) Hydrodesulfurisation = process by which sulfur is catalytically removed from refined petroleum, ~~so that it can react with~~ by reacting it with H_2 to form H_2S. v. toxic, so it is trapped and broken down into elemental sulfur to manufacture H_2SO_4.

2) Alternatives - lower demand for fossil fuels
- more efficient energy transfer systems
- Switching to~~more~~ renewable energy

3) Liming of lakes - neutralises acid and increases concentration of Ca^+ and CO_3^{2-}, good for coral

Ka and Kb [Again]

- Consider the c. base - acid pair HA / A^-

$HA \rightleftharpoons H^+ + A^- \rightarrow K_a = \frac{[H^+][A^-]}{[HA]}$

$A^- + H_2O \rightleftharpoons HA + OH^- \longrightarrow K_b = \frac{[HA][OH^-]}{[A^-]}$

$\therefore K_a \cdot K_b = \frac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} \cdot \frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}}$

$K_a \cdot K_b = [H^+][OH^-] = K_w \quad \therefore \boxed{pK_a + pK_b = pK_w}$ for c. acid / base pair

This is ~~quatat~~ quantitative proof that stronger acids ~~disassociate~~ have weak c.bases because, if pka is low, pKb must be high [∴ con base is weak]

Buffers

Example Q : Describe how a phosphate buffer [~~(a)~~ $H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq)$] minimises the effect of the addition of (a) a strong base, (b) a strong acid

(a) OH^- reacts with $H_2PO_4^-$ to form HPO_4^{2-} and H_2O, minimising the effect of this addition

$$H_2PO_4^- + OH^- \rightarrow H_2O + HPO_4^{2-}$$

(b) H^+ reacts with HPO_4^{2-} to form $H_2PO_4^-$, minimising the effect of this addition

$$H^+(aq) + HPO_4^{2-}(aq) \rightarrow H_2PO_4^-(aq)$$

Kw, Ka and Kb

Example Q : Why does a v. acidic solution still have OH^- ions?

$[OH^-]$ cannot go to 0 because there is an equilibrium present such that $[OH^-] = \frac{K_w}{[H^+]}$, thus $[OH^-] \neq 0$

General Tips + Notes

1) ALWAYS. WRITE. EQUATIONS
2) Refer to the reactions in explaining how buffer solutions resist change
3) Always divide moles by volume for everything
4) State, in a titration question, the acid base combo in terms of strength
5) To find proportions of salt and acid → use Ka

e.g 9.50 pH Buffer required with NH_3 and NH_4Cl

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$\frac{K_b}{[OH^-]} = \frac{[NH_4^+]}{[NH_3]}$$ → find ratio, then deduce vol needed, can get directly if concs are already equal

$$pH = pKa + \log\left(\frac{[salt]}{[acid]}\right).$$

$$pOH = pK_b + \log\left(\frac{[salt]}{[base]}\right).$$

$4.50 = 4.25 + \log\left(\frac{salt}{base}\right)$. $\log\left(\frac{salt}{base}\right) = ~~lg~~(0.25)$. $= 10^{-0.25}$ $= ~~0.62~~$.

$= 5.62 \times 10^{-1}$.

Write notes for thiosulfate titrations + $KMnO_4$'s

Chapter 9: Redox Reactions

Oxidation
1) loss of e^-
2) gain of O
3) loss of H

Reduction
1) gain of e^-
2) loss of O
3) gain of H

An oxidising agent induces oxidation in another compound, while the agent is reduced → [electron acceptor]

A reducing agent induces reduction in another compound, but in itself is ~~reduced~~ oxidised [electron donor]

Rules
1) In its elemental state (e.g S_8), the element's oxidation state is zero.
2) A monoatomic ion's oxidation state = the charge on it
3) Overall charge on a polyatomic ion = ~~th~~ total sum of all oxidation numbers
4) Oxygen is always -2, unless in peroxides (H_2O_2) or superoxides (Na_2O_2). [∗ -1]
5) Hydrogen is always $+1$, unless in metal hydrides [e.g LiH], [-1]
6) F is always -1

Finding Oxidation States

E.g 1) CH_2F_2 ← H always +1, F always −1, and total o no. is 0
[x][+1][−1]

let x be o no. of new atom → $x + 2 - 2 = 0$

$x = 0$

Eg 2) $Cr_2O_7^{2-}$ ← O alway −2, and total = −2, ∴ let Cr's oxidation number = x

$$2x + (-2)(7) = -2$$
$$2x - 14 = -2$$
$$2x = \cancel{-16}\ 12$$
$$x = +6$$

Naming compounds

E.g 1 = $CuCl_2$ ← we can see that Cu's oxidation state = (+2)
[+2] [−1]
So, we write this compound as copper (II) sulfate

E.g = $CoSO_4$ ← Co's oxidation state is (+2) so we write it as Cobalt (II) sulfate.

A species oxidised in redox ~~loses~~ ~~dec~~ increases in oxidation number, a species reduced decreases in oxidation number.

$$\underset{[+2]}{Cu^{2+}_{(aq)}} + \underset{[0]}{Zn_{(s)}} \rightarrow \underset{[+2]}{Zn^{2+}_{(aq)}} + \underset{[0]}{Cu_{(s)}}$$

oxidation

reduction

$$2\,\underset{[+7]}{MnO_4^-} + 16H^+ + \underset{[-1]}{10Cl^-} \rightarrow \underset{[+2]}{2Mn^{2+}} + 8H_2O + \underset{[0]}{5Cl_2}$$

reduction

oxidation

Redox Half Equations

Most of the redox equations we encounter can be split into half equations

Take: $Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Can't we just split it into

~~Cu~~ $Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$

and

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$

↓ if combined,

we cancel out the e^- or any other similar quantities

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

Example 2: A reaction between MnO_4^- and ~~[illegible]~~ Cr^{3+} to form ~~$Cr_2O_7^{2-}$~~ $Cr_2O_7^{2-}$ and Mn^{2+}

MnO_4 must go to Mn^{2+}, which differs by 4 Os

Therefore, we add H^+ ions to RHS so the 4Os form water

$$\underset{[+7]}{MnO_4^-} + H^+ \rightarrow \underset{[+2]}{Mn^{2+}} + H_2O$$

Note that this is a reduction, so we must add the difference in oxi numbers to LHS

$$MnO_4^- + \boxed{5e^-} + 8H^+ \rightarrow Mn^{2+} + \overset{4}{\cancel{8}}H_2O$$

we now balance the H^+s and H_2Os with respect to fixed number of oxygen

Cr^{3+} to $Cr_2O_7^{2-}$
[+3] ⟷ [+6]

$Cr_2O_7^{2-}$ to Cr^{3+}
[+6]

Cr^{3+} to $Cr_2O_7^{2-}$

$$\underbrace{[+3] \qquad [+6]}$$

↑ oxi number, therefore oxidation. So we add the diff in oxi to LHS but ×2 because 2 Cr atoms in final

$$2Cr^{3+} + \underline{7H_2O} \rightarrow Cr_2O_7^{2-} + \underline{14H^+} + \boxed{6e^-}$$

H₂O and H⁺ added to give O that is needed for $Cr_2O_7^{2-}$. It is balanced with respect to final no of oxygen atoms

HOLD-UP!

We have $6e^-$ being produced in the oxidation and only 5 being used in the reduction. We need to this equal. So, we do the lowest common multiple, which is in this case 30.

$$[2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-] \times 5$$

$$10Cr^{3+} + \boxed{35H_2O} \rightarrow 5Cr_2O_7^{2-} + \boxed{70H^+} + \boxed{30e^-}$$

$$[MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O] \times 6$$

$$6MnO_4^- + \boxed{30e^-} + \boxed{48H^+} \rightarrow 6Mn^{2+} + \boxed{24H_2O}$$

−

because 70 prod at start, only 48 used, leave 22 H at end poin

$$6MnO_4^- + 10Cr^{3+} + 11H_2O \rightarrow 5Cr_2O_7^- + 22H^+ + 6Mn^{2+}$$

↑ because 35 used at the start but we also produce 24 at the end, the net used H₂O is therefore 35 − 24 = 11

Doing the equations

1) Give a full equation for $\overset{[+6]}{H_2SO_4}$ to $\overset{[0]}{S}$

1) Identify change in oxi state. It is +6 to 0, hence a reduction occurs

2) We need a source for the electrons, so let's take a strong reducing agent, i.e low FIE.

because 6e⁻ needed →

$$\boxed{6}[Na(s) \rightleftharpoons Na^+(aq) + e^-]$$

3) Now, let's consider the change from H_2SO_4 to S. The H_2O_4 needs to go out, but as water.

$$6e^- + H_2SO_4(aq) + 6H^+ \longrightarrow 4H_2O(l) + S(s)$$

↑ because more H⁺ needed for H : O = 2 : 1

4) Combine using sorcery

$$6Na(s) + H_2SO_4(aq) + 6H^+(aq) \longrightarrow 4H_2O(l) + 6Na^+(aq) + S(s)$$

Feasability of certain reactions

Why doesn't this reaction happen? $\underset{\substack{\uparrow \\ \text{would have to be oxidised}}}{\underline{Cu}}(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$

$Zn > Cu$ in terms of it's ability to lose its electrons, so it is more energetically favourable for it to lose the e^-, not Cu. Metals higher in terms of their ability to oxidise can therefore displace less capable metals in their ions. The order (in descending) of decreasing reducting agents is the reactivity series

Redox titrations

- We can use redox titrations to find the concentration of certain chemicals and

E.g 1) A solution contains both Fe^{2+} and Fe^{3+} ions. A $50cm^3$ sample of the solution is titrated with 35.0ml of 0.00280 mol/dm³ $KMnO_4$, which oxidises Fe^{2+} to Fe^{3+}. The permanganate ion is reduced to Mn^{2+}. Another $50cm^3$ sample is treated with zinc that reduces all Fe^{3+} to Fe^{2+}. The resulting solution is then titrated with 0.00280 moldm⁻³ $KMnO_4$, but 48.0ml is needed. Find $[Fe^{2+}]$ and $[Fe^{3+}]$

1) Let's consider the first reaction. $Fe^{2+} \rightarrow Fe^{3+} + e^-$

and

$$5e^- + \overset{[+7]}{MnO_4^-} \rightarrow Mn^{2+}$$

$\therefore$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

and

$$5Fe^{2+} \rightarrow \cancel{3}Fe^{3+} + 5e^-$$

so,

$$MnO_4^- + 8H^+ + 2Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

2) Now we can do a ICE (ICE BABY) table.

$$MnO_4^- + 8H^+ + \overset{5}{\cancel{2}}Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

I $\left[0.00280 \times \frac{35}{1000}\right]$ = 0.000098 mol $\quad \downarrow \therefore$ 0.000490

Fe^{2+} mol = ~~0.000146 mol~~

$$[Fe^{2+}] = \frac{0.000\cancel{146}490 \text{ mol}}{0.05 dm^3} = \overset{0.00980}{\cancel{0.00392}} moldm^{-3}$$

3) Let's find total moles of Fe^{2+} and Fe^{3+} by using the titration of MnO_4^- and Fe^{2+} again. $\therefore$ ~~$[Fe^{3+}]$~~

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

I 0.0001344 $\qquad$ 0.000672 moles

0.000672 − 0.000490 = 0.000182

$[Fe^{3+}]$ = 0.00364 moldm⁻³

Winkler Method

- Used to measure Biological Oxygen Demand
- This measures dissolved oxygen in ppm required to decompose organic matter over a set period of time
- Initially saturated with oxygen, so we know first conc
- Later, we take a sample
- We react it as follows

1) $2Mn^{2+}(aq) + \boxed{4OH^-} + O_2(aq) \rightarrow 2MnO_2(s) + 2H_2O(l)$ ← alkaline conditions
2) KI is then added → $MnO_2(s) + 2I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 2H_2O(l)$
3) Then titrated with $Na_2S_2O_3$. $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

Example: all solutions used were ~~1mol~~ 1×10^{-2} mol dm^{-3}, 6cm^3 $Na_2S_2O_3$ reacted with all the iodine, using starch as an indicator. When clear, all I reacted. Find $[O_2]$ in ppm. The sample was 100 cm^3

m ~~Na~~$S_2O_3^{2-}$ → $1\times10^{-2} \times \frac{6}{1000} = 6\times10^{-5}$ mol

moles of I_2 ∴ = 3×10^{-5} mol (according to eqn it is $\frac{1}{2}$ of m ~~Na~~$S_2O_3^{2-}$)

moles of ~~[illegible]~~ $Mn^{2+}O_2$ → 3×10^{-5} mol

∴ moles of $O_2(aq) = 1.5\times10^{-5}$ mol

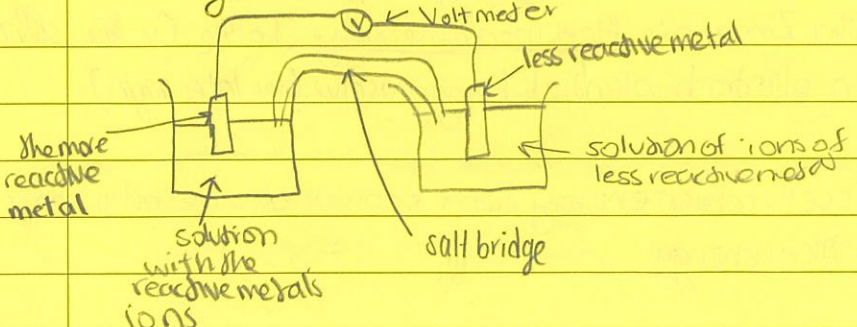
Note: ppm = $\frac{g}{dm^3}$

$[O_2(aq)] = \frac{1.5\times10^{-5}\text{mol} \times 32}{0.100\text{dm}^3}$ ← finding O_2 mass here

$= 4.8$ ppm

Voltaic (galvanic cells)

- convert energy from spontaneous, exothermic chemical processes to electrical energy
- Basically, it looks like this



- Anode is on the left, cathode on right
- The anode electrode is the metal that oxidises more readily i.e if $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$, equilibri lies to LHS.
- The cathode is where reduction occurs, where the metal is more likely to be reduced than oxidised so ie, $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$, equil lies to reduced form, so RHS,

Terms

Half cell: a metal in contact with an aqueous solution of its own ions

Voltaic Cell: 2 half cells connected together

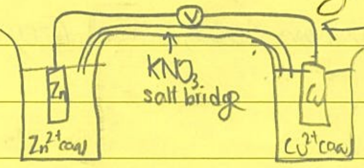
Why is a salt bridge needed?

1) complete circuit
2) allow movement of ions between electrolytes
3) keep electrical neutrality

- to complete the circuit + maintain PD.
- keeps half cells electrically neutral. The anode develops a positive charge because of the loss of e⁻, so the negative ions in a salt bridge flow to it to maintain neutrality
- Cathode develops a negative charge because of a build up of e⁻, hence cations in salt bridge move into the cathode half cell
- Usually a porous substance with an ~~son~~ ionic compound [so can diss in solution) that has inert ions so there are no new reactions in either half cell, no interference

How do we generate electrical energy?

- Let us consider the following example.



we need the metal wire to facilitate the flow of e⁻

Observations
1) paler colour in electrolyte being reduced
2) increase in size of cathode
3) decrease anode size

1) In the Zn half cell, Zinc atoms form ions by being oxidised, releasing electrons, that make the electrode negatively charged with respect to the solution
2) This creates a charge seperation, known as ~~a th~~ electrode potential between the $Zn^{2+}(aq)$ and Zn atoms. This creates the following equil. $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$

NOTE: We write all half cell equations as reduction because it's standard.

3) Looking at a data booklet, we can see that the standard electrode potential of Zn(s) [E°] is −0.76V. This indicates that the oxidation reaction is favoured.
4) The ~~ch~~ electrode potential of the copper is +ve on the other hand, so the reduction reaction is favoured. $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$. This is because there are fewer e⁻ in the Cu(s) so we have a lower charge seperation.
5) Therefore, the electrons from the Zinc anode flow spontaneously to the Cu ~~to~~ cathode because of the difference in electrode potentials being positive. (see later pages)

Syllabus Key Phrase: Voltaic cells convert energy from spontaneous exothermic chemical reactions to electrical energy

6) We then write the reactions

Cathode

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu(s)$

Anode

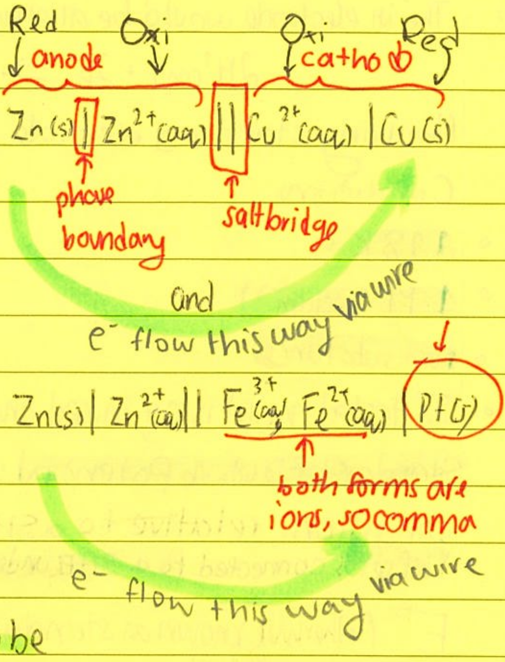
$Zn^{\cancel{2+}}(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Net

$Cu^{2+}_{(aq)} + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Writing notations

- single vertical line seperating different states of matter
- double vertical line for salt bridge
- aqeous ions adjacent to salt bridge
- Anode on left, cathode on right
- No spectator ion
- If same phase, ~~sp~~ seperated by comma
- Pt electrodes used if the ~~cathode/anode~~ redox used has reduced + oxidised form in aq.
- We label the Pt as the anode or cathode in such a case



Recall: the metal higher on reactivity series with more negative $E^\ominus$ is the anode as it is more likely to be ~~reduced~~ oxidised and the other has a higher reducing power. ~~hence it has a~~

VIP

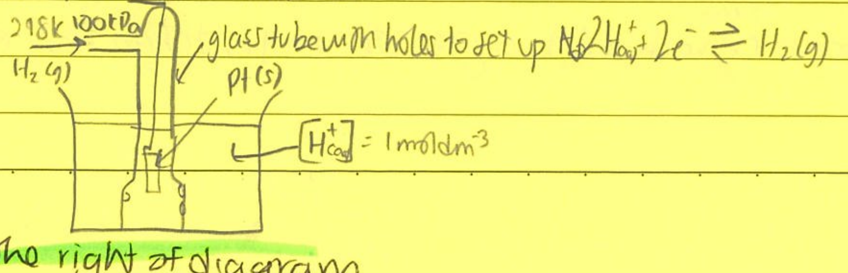
- electrons move from anode to cathode via the external circuit
- anions migrate from the ~~salt bridge to the cat~~ cathode to the anode via salt bridge
- cations migrade from the anode to the cathode via salt bridge

Electromotive force

- A voltaic cell generates a potential difference dubbed electromotive force
- One ~~is~~ half cell with negative electrode potential, another with a positive electrode potential. This generate EMF, which causes the movement of e⁻ from anode to cathode
- EMF = E_{cell}

Standard Hydrogen Electrode (SHE)

- consists of an inert electrode, usually $Pt_{(s)}$ in contact with $1\,mol\,dm^{-3}$ H^+ [e.g in 1 M HCl]
- 100kPA and 298 K
- $E^\ominus$ (standard electrode potential) of SHE = 0



- always placed to the right of diagram

- Pt(s) used because it is inert and catylses the proton reduction to $H_2(g)$
- The ~~in~~ electrode would be alternatively bathed in $H_2(g)$ and $H^+_{(aq)}$ setting up an equilibrium

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

Measuring standard electrode potentials

Conditions

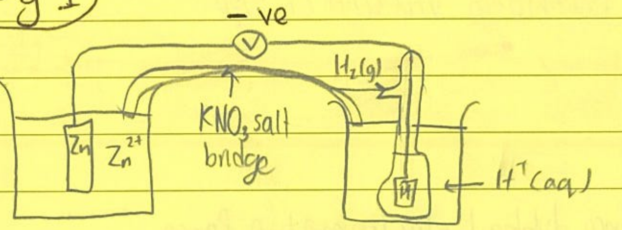
- 298K
- 1 M ($moldm^{-3}$)
- Pure substances
- If tested metal is aq, in red and oxi form, Pt(s) electrode used

Standard Electrode Potential: Voltage of the reduction half equation under standard conditions, relative to a SHE, Better: the potental difference obtained when a half cell is connected to a SHE under standard conditions

$E^{\ominus}$ (otherwise known as standard reduction potentials)

- If +, the metal reduces to a greater extent than the hydrogen, so its equilibrium would lie to the RHS. e^- flow from H here
- If −, the metal oxidises to a greater extent and less for red than H so equil favours LHS. e^- flows to H here.

Eg 1



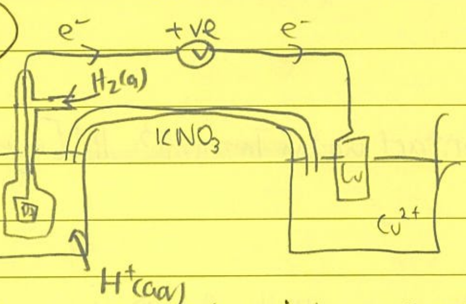
$Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-$
$2H^+_{(aq)} + 2e^- \rightarrow H_2(g)$ $\therefore$ $Zn(s) + 2H^+(aq) \rightarrow H_2(g) + Zn^{2+}(aq)$

$Zn(s) | Zn^{2+}(aq) || H^+(aq) | H_2(g) | Pt(s)$

$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn(s)$
$2H^+_{(aq)} + 2e^- \rightleftharpoons H_2(g)$

− ve value demonstrates Zincs greater ability to lose e^- relative to Hydrogen.
$\therefore$ Zn on LHS for the notation as e^- flow to H

Eg2



$2H^+_{(aq)} + 2e^- \rightleftharpoons H_2(g)$
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu^{\cancel{2-}}(s)$

$Pt(s) | H_2(g) | H^+(aq) || Cu^{2+}(aq) | Cu(s)$
$\therefore$ Net = $H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+(aq) + Cu(s)$

+ve because Cu reduced to a greater extent than H $\therefore$ e^- go from H

Finding $E^\ominus_{cell}$

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$

Think about it this way. We always know $E^\ominus$ of a metal when it acts as a cathode, so $E^\ominus_{anode} = -E^\ominus_{cathode}$ because e^- flow in opposite direction of PD is reversed.

e.g Find E_{cell} of the Zn and Cu half cell

$Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu(s)$

~~$E^\ominus_{Zn} = -0.76$~~

~~$E^\ominus$~~

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\ominus = -0.76V$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\ominus = +0.34V$

we flip this to find $E^\ominus$ for oxi

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^- \quad E^\ominus = 0.76$

$\therefore$

$E_{cell} = 0.34 + 0.76$

$= 1.10V$

~~e.g 2. Find $E^\ominus$ of Ag if $E^\ominus_{cell} = 1.25$ with H~~

A $E^\ominus$ that is + and ↑ is a good oxidising agent, a $E^\ominus$ that is −ve and very low (e.g −1000) is a good reducing agent. e^- flow to cell with highest +ve $E^\ominus$

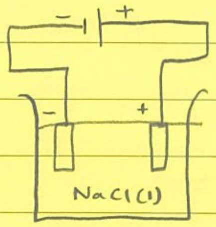
A $-E^\ominus$ cell simply means that electrons flow from that electrode / is a better reducing agent than the other electrode (if the other is +ve)

Free Energy and Spontanuity

- We can relate ΔG to $E^\ominus$ by $\Delta G = -nFE^\ominus$, where F is the Faraday constant, which is 96,500 coloumbs per mole, and n is number of moles of e^- transfered [just use coefficient]
- Therefore, if we have + $E^\ominus_{cell}$, the reaction is spontaneous, requires no additional energy other than E_a, so could occur in a test tube
- If we have a negative $E^\ominus_{cell}$, ΔG is positive, so the reaction is not spontaneous.
- Could only proceed with an external energy soure to force the reaction to occur in the reverse [so e^- flow to cathode]

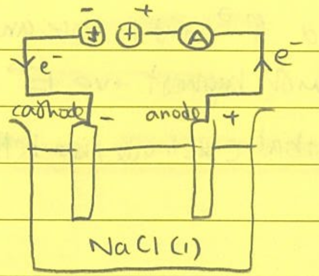
Electrolytic Cells

- convert electrical energy to chemical energy, by way of non-spontaneous processes
- Oxidation still occurs at the anode and reduction at the cathode
- However, given that a electrolytic cell looks like this



- the −ve electrode can donate e^- to the species to be reduced and the positive electrode attracts electrons from the species to be oxidised
- Hence, the −ve electrode = cathode and +ve electrode = anode
- electricity is passed through an electrolyte, a substance that does not conduct electricity in solid form, but can in aq or l
- It is decomposed in the process
- We can get reactive metals from common ores → e.g Al(s) or Fe(s)
- Take Na for instance, v. high on reactivity series, to produce Na(s), we need an even stronger reducing agent

Example



Summary (markscheme)

- Na^+ move to cathode, Cl^- move to anode
- In the anode, electrons are released from Cl^- (oxidation)
- Accepted from the ~~a~~ cathode by the Na^+ ions [reduction]
- $Na^+(l)$ reduced, $Cl^-(l)$ oxidised
- $2Na^+(l) + 2e^- \rightarrow 2Na(s)$
- $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
- * Current because of the movement of electrons through the external circuit and the movement of ions in electrolyte

- anions oxidised at anode (+)
- cations ~~ar~~ reduced at cathode

① = if oxygen evolved, anode has a lower ph (acidic)

Observations to write

② = if $H_2(g)$ evolved, cathode region ~~acidic~~ alkaline as ↑$[OH^-]$

1) ↑①$[OH^-]$/↓ or ②↑$[H^+]$/↓, then note pH ↑ or ↓ [effervescence]
2) Colour of gases or metals produced
3) ~~a~~ Cl identified by bleaching damp blue litmus paper
4) Possible app of molar ratios

Electrolysis of Aqeueous solutions

- we can have H_2O oxidised to O_2 at anode [~~[illegible]~~ $\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq)$]
- and we can have H_2O reduced to $H_2(g)$ at cathode [$H_2O(l) + e^- \rightleftharpoons H_2(g) + OH^-(aq)$]
- This only would happen if E° cell of these oxidations and reductions are higher than the other ions. What I mean is this. Consider the reduction to H_2. It has E° ~~cell~~ of − 0.83V
- If the other ion is Pb^{2+} [whose reduction is E° = −0.13], H_2 produced because |E°| is higher for H_2O reduction. So H_2O is a better oxidising agent than Pb^{2+}
- Consider the anode, where O_2 produced [~~[illegible]~~ $\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq)$) with E° = 0.40 for reduction, ~~but oxidation is − 0.40V.~~
- ~~This is why in electrolysis of $NiCl_2$, nickel not formed as E° = −0.26, for Ni^{2+} E° > for H_2O oxidation, therefore H_2O stronger weaker oxidising reducing agent~~
- ~~This E° is greater than that for the~~ K^+ reduction, so it is more likely for K to be reduced ~~instead of~~
- If we have Sn for example, more likely to oxidise than

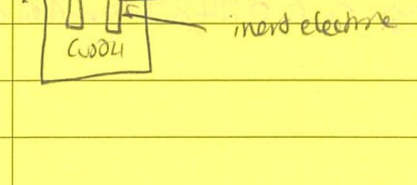
$$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$$

$$2H_2O(l) + O_2(g) + 4e^- \rightleftharpoons \overset{4}{\cancel{2}}OH^-(aq)$$

To Sum Up!

- If E° is lower than E° of the $H_2O(l) + e^- \rightleftharpoons \frac{1}{2}H_2(g) + OH^-(aq)$ [i.e more −ve], ~~the species will be reduced and no H_2O produced as the species is a stronger~~ H_2O is a stronger oxidising agent [as it has ↑ E°] and will be reduced as opposed to the species
- If E° is greater than E° of ~~$O_2(g)$~~ $\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq)$, the ~~$H_2O$~~ OH^- is a stronger reducing agent than the species, so ~~it is~~ O_2 is produced, not the species

Example!



Why is Cu(s) deposited?

- Cu^{2+} is a stronger oxidising agent than H_2O and hence is deposited / displaced to form Cu(s)

Why is $O_2(g)$ formed?

- SO_4^{2-} weaker reducing agent than ~~H_2O~~ OH^- so OH^- decomposes into $O_2(g)$
- Note that pH ↓ because ↑ pOH.

Ion Concentration

- If one ion is more concentrated than another, it will be selectively discharged
- E.g conc ~~C~~. NaCl would produce Cl_2 gas rather than O_2 at ~~ca~~ anode because ↑ $[Cl^-]$ than ~~$[OH^-]$, so more it would be discharged. In dilute, O_2 evolved because ~~H~~ OH^- stronger reducing agent than Cl^- normally~~ shifts this equil $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$ to RHS, ↑ e^- that can flow so ↓ E° and therefore becomes a stronger reducing agent than OH^- so selectively discharged

Electrodes

- if we have $Cu^{2+}_{(aq)}$ in sol and use $Cu_{(s)}$ electrodes, +ve electrode is oxidised to release e^- and form $Cu^{2+}_{(aq)}$
- $Cu_{(s)}$ simultaneously deposited at cathode, so no conc change → stays constant
- Same sit if we have a metal as electrode and it's ion in electrolyte

Factors affecting Quantities of Products

1) Current - ↑ current, increased flow of charge and e^-. E.g if doubled, 2x amount of electrons flowing through system, 2x as ~~many~~ much products formed. If time is doubled, 2x as many e^- flow through, so 2x as much product

Recall

$C = A \times t$ = Coulomb = current × time (s)

and $F = 96{,}500\ C\,mol^{-1}$ so $\frac{C}{F}$ = moles of e^- flowing

Example

(a) How many grams of Cu are formed on cathode of an electrolytic cell holding $CuCl_{2(aq)}$ with 2.00 A current for 2 min

(b) what if $CuCl_{(aq)}$ used.

① Find C → $C = A \cdot t$

$C = 2 \cdot 120$

$= \underline{240C}$

① This time it is $Cu^+ + e^- \rightarrow Cu_{(s)}$
So you need less moles of e^- to produce $Cu_{(s)}$, ergo more $Cu_{(s)}$ would be produced

② Find moles → ~~2x~~ $\frac{C}{F}$ = moles = $\frac{240C}{96{,}500\,C\,mol^{-1}}$ ≈ 0.0024870 moles of e^-

③ Look at Eqn for Cu

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

∴ If 0.0024870 moles of e^- → moles of $Cu_{(s)}$ = $\frac{1}{2}$ mol of e^-
≈ 0.00124 mol

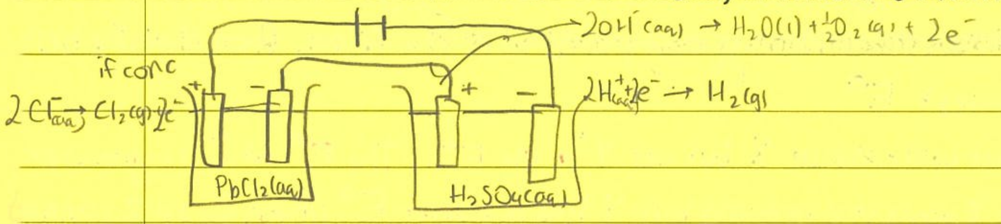
④ Find mass

$0.00124 \cdot 63.55 = \underline{\underline{0.0790g}}$

② Ion Charge

- If ↑ + charge, more moles of electrons needed to reduce to make one mole of metal
- ∴ as ↑ charge, mass of prod formed ↓, (assuming relative to a lower cation at same current + time)

Note: Cells in series like the one below, ensure same amount of e^- flow to each electrode



Relative amounts of products

$Cl_2 : Pb : O_2 : H_2$ → if you think about, for $4e^-$, 2 moles of $H_{2(g)}$, $Pb_{(s)}$ and $Cl_{2(g)}$ produced but only 1 mole of $O_{2(g)}$.
$2 : 2 : \boxed{1} : 2$

↑
$\frac{1}{2}O_{2(g)}$ for $2e^-$, the rest all 1 for $2e^-$

Electroplating

Def: Process of using electrolysis to deposit a layer of metal onto a conductive object

Requires 1) An electrolyte with the ions of the metal to plate with
2) ~~a~~ the thing to be plated is on the cathode
3) Anode can be of same metal to continuously replenish supply of ions

Purpose: Decorative: silver plated utensils
Corrosion: Fe with zinc layer is galvanised Iron and is ∴ protected from corrosion

Concentration and ~~Electrolysis~~ Voltaic Cells

- To assess the impact of a concentration or T change, we need to look at the reduction or oxidation reaction. E.g if $[Hg^{2+}]$↑, we look at $Hg_{(l)} \rightleftharpoons Hg^{2+}_{(aq)} + e^-$.
- Then observe equil. If for oxi, shift to side with fewer e^-, ↑ $E^\ominus_{reduction}$, so looking at E_{cell}, E_{cell} ↓ provided no change in other factor. Recall the Hg example, equil shifts to favour reduction so ↓ $E^\ominus_{cell}$
- If for reduction, a shift to the ~~reduction~~ oxidation reaction ~~increases~~ decreases Ered and a shift to favour red ↑ Ered, so ↓ Ecell and ↑ Ecell respectively

Question Feedback

- If asked for best reducing/oxidising agent, use these phrases [if asked in terms of e^-]
  - best reducing agent = greatest tendency to lose electrons
  - best oxidising agent = greatest tendency to gain electrons
- "State and explain the symbol of ΔG" → -ve or +ve and then spontaneous or not
- In sacrificial protection, the layer that is a better reducing agent than Fe is optimal. This is because it will be oxidised preferentially compared to ~~as~~ the Fe (s). Recall that the best reducing agent has the lowest $E^\ominus$
- "Identify a substance that will oxidise X but not Y" → use $E^\ominus$. The $E^\ominus$ of Z is greater than X, so it will oxidise X while it is reduced but Y has a higher $E^\ominus$ than Z, so Z cannot oxidise it. The E° value of the oxidation of X by Z is positive, whereas for oxidation of Y by Z, it is negative because $\overset{Y}{\cancel{X}}$ is a stronger oxidising agent than ~~X~~ Z
- 5 things for a SHE → 1 atm $H_2(g)$, 298 K, Pt electrodes, 1 mol dm^{-3} [$H^+(aq)$]

If electrical conductivity is discussed on a redox question, do standard answer but then say cations move to cathode + anions to anode

10: Organic Chemistry → the Chemistry of Carbon

C D23

a.k.a fake biology

Date No.

Homologous Series

- Definition: a series of compounds of the same family, with the same general formula and differ from one another by a common structural unit.
- varying carbon backbone lengths, from C_1 to C_∞, increasing by CH_2
- similar chemical properties as same functional groups presents
- There is a gradual and progressive change in physical properties
- E.g Boiling Points → as the size of a molecule increases, the size of a random instantaneous dipole increases, hence the strength of LDFs increase as you ascend a homologous series. Therefore, more energy is required to break the stronger intermolecular forces

Identifying Compounds

- identify longest carbon chain first [e.g $CH_3CH(CH_3)CH_2CH_3$, longest chain is 4 Cs and 1 methyl, ∴ it is something-butane]
- Bonding → all single bonds → -ane, one double = -ene, one triple -yn-.
- Check functional group [see detailed list on next page]

① alkene $C{=}C$ → -ene

② alkane $C-C$ → -ane

③ Alcohol $C-OH$ → -ol

④ Carboxylic Acid $C\begin{smallmatrix}=O\\-O-H\end{smallmatrix}$ → ~~[illegible]~~-oic acid

⑤ Haloalkane $\overset{\cdot\cdot}{C}-C-\underset{\cdot\cdot}{\overset{\cdot\cdot}{H}}\colon$ → iodo/bromo/chloro/fluoro-

⑥ aldehyde $\underset{\underset{O}{\|}}{C}-H$ [at chain end] → -al

⑦ ketone O $C-\overset{\overset{O}{\|}}{C}-C$ [not at end] → -one

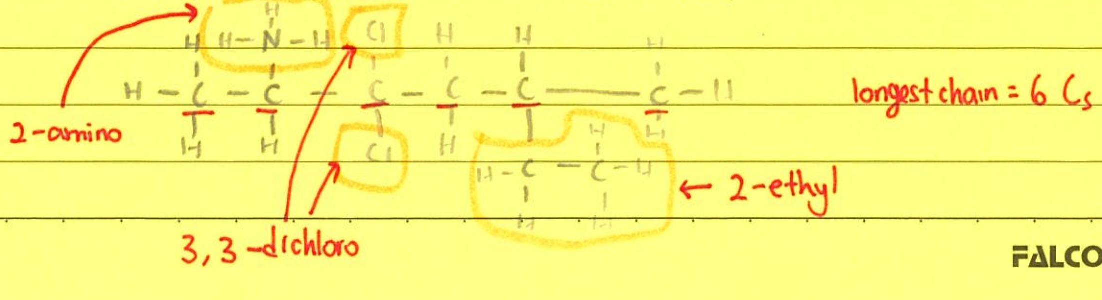
⑧ Amide $-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-H$ → -amide [if at end]

⑨ Amino $-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-$ → amino-

- Put numbers ~~→~~ ~~e.g~~ alcohols → position of OH → propan-1-ol, alkenes, position of $C{=}C$, prop-1-ene halo alkanes → position of halogen(s), 1-bromopropane

Example: $CH_3CH[NH_2]C\cancel{H}(Cl)(Cl)CH_2CH(C_2H_5)CH_3$

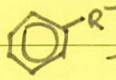
Let's draw it



∴

2

Functional Groups

1) ~~Alkane~~ Alkene [$C=C$] → alkenyl
2) Alkyne [$-C\equiv C-$] → alkynyl
3) Alcohol [$C-OH$] - hydroxyl
4) Ether [$R-O-R'$] → -oxy(alkane), where alkane is R' e.g ethoxyethane
5) ketone [$-\overset{O}{\overset{\|}{C}}-$] -none
6) Aldehyde [$-C\substack{\nearrow O\\ \searrow H}$] -al
7) carboxylic acid [$C\substack{\nearrow O\\ \searrow OH}$]
8) ester [$-\overset{O}{\overset{\|}{C}}-O-C-$]
9) nitrile [$-C\equiv N$] [alkane including last carbon - nitrile]
8) amine [$C\overset{\nearrow O}{}-N\substack{\nearrow H\\ \searrow H}$] [alkane - an amide] e.g propanamide
9) Arene [] [R-benzene], e.g methyl benzene

Homologous series differ by a CH_2

If we have a compound with 2 functional groups, example: an ethane with 2 hydroxyl groups, then it is ethane-1,2-diol. So we keep the alkane bit

Alkanes

Date No.

- comprised purely of C-C and C-H bonds
- only react in presence of energy source because of relatively high bond enthalpies
- Nonpolar because of low electronegativity difference
- Low reactivity due to inability to attract other species, no double bonds or -ve/+ves
- Undergo combustion, cracking + halogenation

Combustion

- The C=O bonds in CO_2 and O-H bonds in H_2O are stronger than C-H and C-C bonds in alkanes, hence $-\Delta H$, ∴ exothermic and releases energy → used as fuel source
- Complete or Incomplete [because of insufficient O_2]

→ $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ [complete]

→ $CH_4 + \frac{3}{2}O_2 \rightarrow \boxed{CO} + 2H_2O$ } [incomplete]

→ $CH_4 + O_2 \rightarrow \boxed{C} + 2H_2O$ }

carcinogenic

binds to haemoglobin to reduce ability to absorb O_2

Halogenation

- occurs by free radical substitution

Note: UV needed

① Initiation

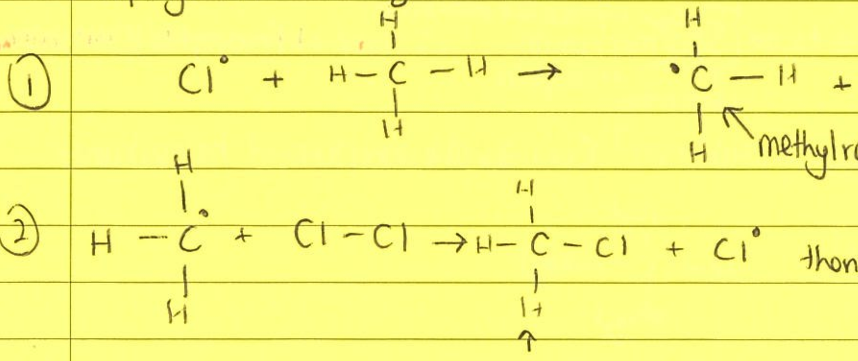
$Cl - Cl \xrightarrow{UV} 2Cl^\bullet$ [homolytic fission → electrons in covalent bond equally shared]

OR

$Cl_2(g) \rightarrow 2Cl^\bullet$

② Propagation = forming more radicals

$Cl^\bullet + CH_4 \rightarrow {}^\bullet CH_3 + HCl$



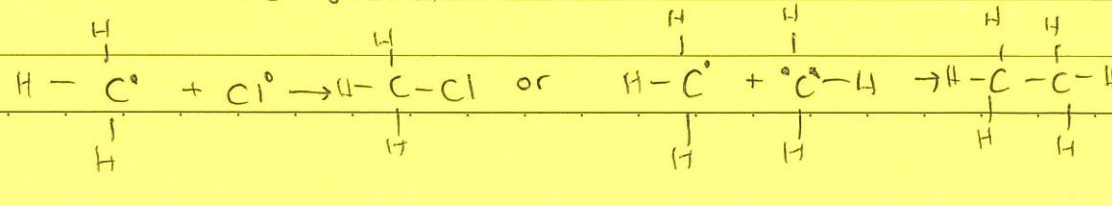
① $Cl^\bullet + CH_4 \rightarrow {}^\bullet CH_3 + HCl$

methylradical, v. reactive

② $CH_3^\bullet + Cl - Cl \rightarrow CH_3Cl + Cl^\bullet$ then step 2 repeated $^\bullet CH_3 + Cl_2 \rightarrow CH_3Cl +$

chloromethane

③ Termination → two radicals react

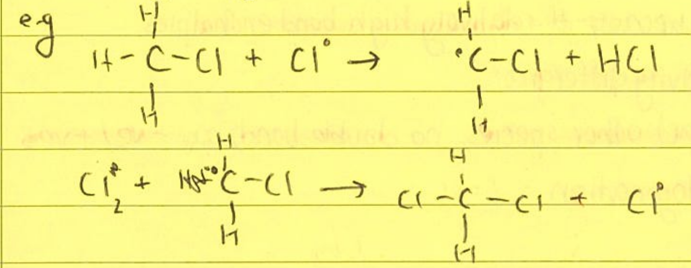


$CH_3^\bullet + Cl^\bullet \rightarrow CH_3Cl$ or $CH_3^\bullet + {}^\bullet CH_3 \rightarrow CH_3-CH_3$

Theoretically, can go further.

Note: The haloalkanes are more reactive than alkanes due to the polarity of the C−X bond, where X = halogen

e.g



$\mathrm{H-\overset{H}{\underset{H}{C}}-Cl + Cl^{\circ} \rightarrow {}^{\bullet}\overset{H}{\underset{H}{C}}-Cl + HCl}$

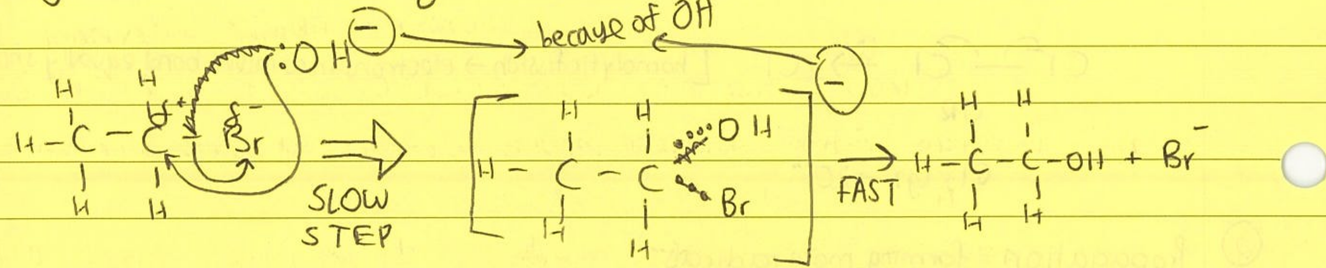
$\mathrm{Cl_2 + {}^{\circ}\overset{H}{\underset{H}{C}}-Cl \longrightarrow Cl-\overset{H}{\underset{H}{C}}-Cl + Cl^{\circ}}$

Overall = $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Nucleophillic Substitution

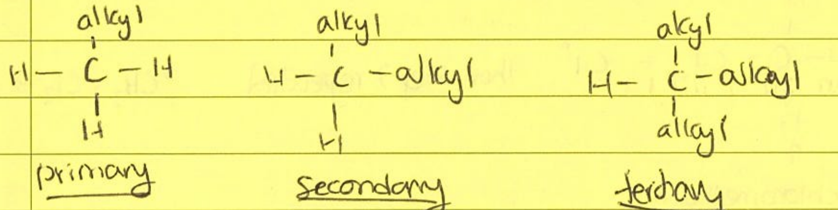
- Nucleophile = an electron rich species, such as a Lewis Base or Ligand, attracted to +ve nuclei
- Attracted to δ^+ on a polar bond. E.g $-\overset{H}{\underset{H}{\overset{\delta+}{C}}}-\overset{\delta-}{F}$
- ~~Halo~~Nucleophile donates a ~~shared~~ lone pair of electrons to the C−F bond, whose electrons (both) move to the δ^- atom. This forms an intermediate in the slow step with a half-broken half formed bond to the halogen and nucleophile. A covalent bond is formed between the ~~covalent bon~~ nucleophile and C, specifically, a dative covalent bond.

Diagram of a substitution by OH^- [S_N2 Mech]



What has been explained relates to an $\underset{\text{substitution}}{\boxed{S}}_{\text{nucleophillic}}\overset{\text{bimolecular slow step}}{2}$ mechanism. ∴ rate = k[nucleophile][haloalkane]

However, what if we have loads of stabilisers? Consider the structures of haloalkanes



primary secondary tertiary

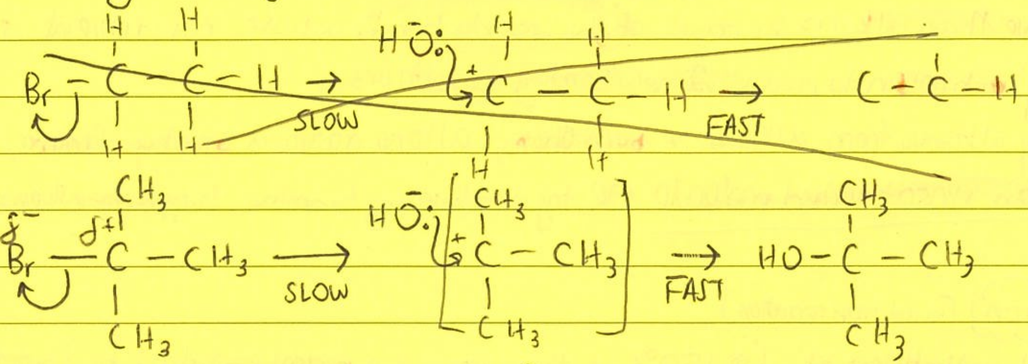
Alkyl groups have an inductive effect, whose electrons move and can stabilise any + charges

Note: S_N1 faster than S_N2, need protic solvent to stabilise carbocation

Tertiary Structures

unimolecular RDS

- most likely to undergo S_N1, because more stable for it



∴ rate = k[haloalkane]

carbocation: the charge on the carbon is stabilised by the inductive effect of the methyl groups → more likely to collide with OH^-

?? ask!!

Secondary haloalkanes can undergo S_N1 or 2. To determine, change [nucleophile], if rate change, S_N2 used. If not; S_N1. *Use aprotic solvent to favour S_N2, because ~~it creates~~ ~~non-polar conditions~~ aprotic solvents [ethoxyethane] favours it. Protic solvents such as water or ethanol support breakdown into carbocations, dissociate into δ^+ and δ^-, latter stabilises +ve C on carbocation

Rates of Reaction

The rate of reactions with haloalkanes vary with the alkane's identity. ~~For example,~~ I > Br > Cl > F. This is because C − I < C − Br < C − Cl < C − F in terms of bond enthalpy. A lower bond enthalpy to be broken requires less energy, ~~ret~~ generating a relatively lower E_a, ∴ ↑ rate of nucleophillic substitution.

The electron density of the nucleophile also affects the rate. ↑ electron density, greater attractive force between nucleophile and δ^+ carbon, ∴ ↑ rate of reaction. ↑ with anions, as it is a negatively charged molecule/ion. This is why OH^- is a better nucleophile than H_2O, because it has a higher electron density

has a

S_N2 is also generally slower than S_N1, because it is a bimolecular RDS, unlike S_N1.

Protic vs Aprotic

Aprotic for S_N2 → this is because protic solvents i.e polar solvents will solvate the nucleophile, rendering it unable to attack the species. Also, because aprotic, no δ^- or −ves to stabilise charge on carbocation, ∴ unlikely to move through S_N1, ∴ S_N2. Aprotic solvate metal cation, ↑ ∴ nucleophile is unsolvated, increasing rate

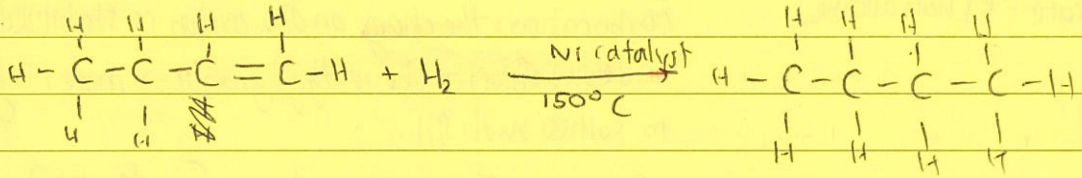
Alkenes

Date No.

- unsaturated hydrocarbons containing a C = C bond
- $C \overset{\pi}{\underset{\sigma}{=}} C$, each C is sp^2 hybridised
- More reactive than alkanes because of the double bond, whose constituent π bond can easily be broken to create 2 new bonding positions
- Distinguishing alkanes from alkenes → burn them, alkene produces a smoky flame, indicates an unsaturated molecule OR try decolourising bromine, happens to alkenes, not alkanes

Hydrogenation [addition reaction]

- alkenes react with $H_2(g)$ at T↑ 150°C in the presence of a nickel catalyst to form alkanes



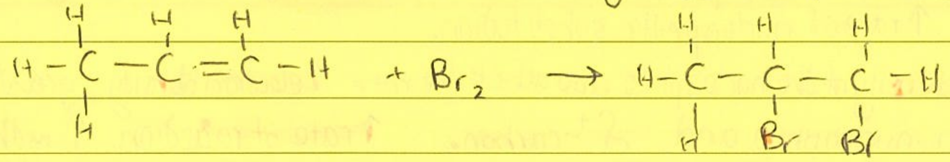
but(1)ene + hydrogen gas → butane

$CH_3CH_2CHCH_2 + H_2 \rightarrow CH_3CH_2CH_2CH_3$

- used to break down oils containing many unsaturated hydrocarbons into saturated compounds with higher b.p and m.p. Allows for margarine to be solid at room temperature

Halogenation [addition reaction]

- react with diatomic halogens to produce dihalogenocompounds
- occur at r. temperature, decolourises the halogen: tests for presence of C=C

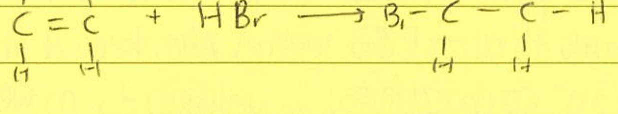


$CH_3CHCH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$

prop(1)ene + bromine → 1,2 dibromopropane

Addition Reactions with Hydrogen Halides [hydrohalogenation]

- react to form haloalkanes, at room temperature



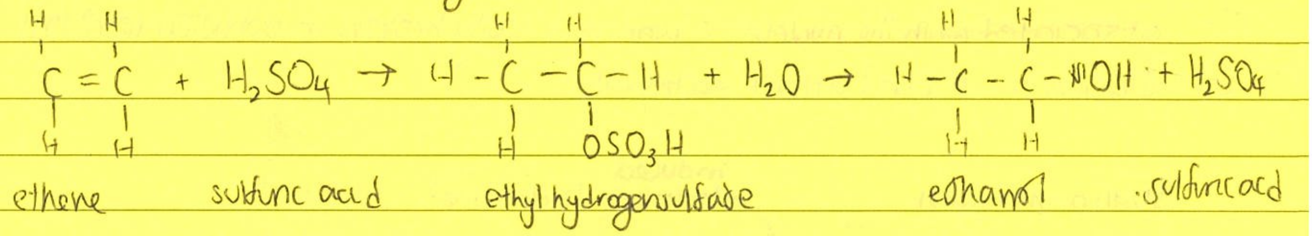
ethene + hydrogen bromide → bromoethane

FALCON

- reactivity ↑ as you descend group 7/VII, because of decreasing H-X bond enthalpy, ↓ E_a, ↑ rate of reaction

Hydration (addition reaction)

- reaction with H_2O to form alcohol using concenorated HCl



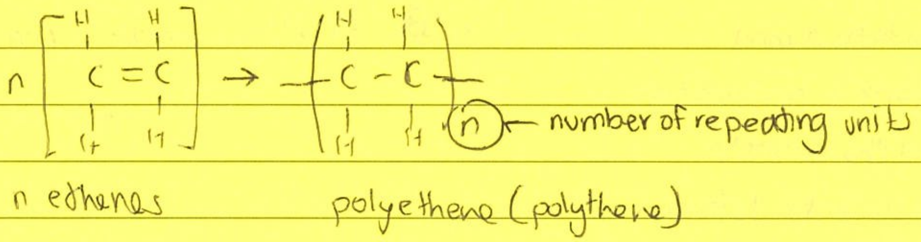
$$H_2C{=}CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_3H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$$

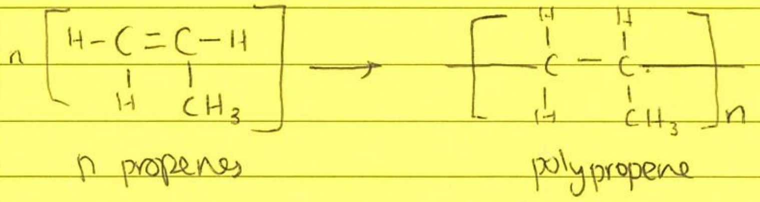
Overall = $C_2H_4 + H_2O \longrightarrow C_2H_5OH$

- need steam as well, ethanol needed as a protic solvent

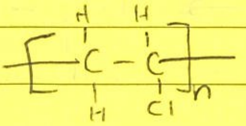
Polymerisation

- a series of addition reactions between identical alkenes
- alkene called the monomers

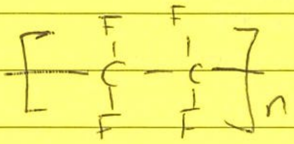




- Poly chloroethene [PVC] →



- Poly[tetrafluroethene] = teflon/PTFE →



8

Electrophillic Addition

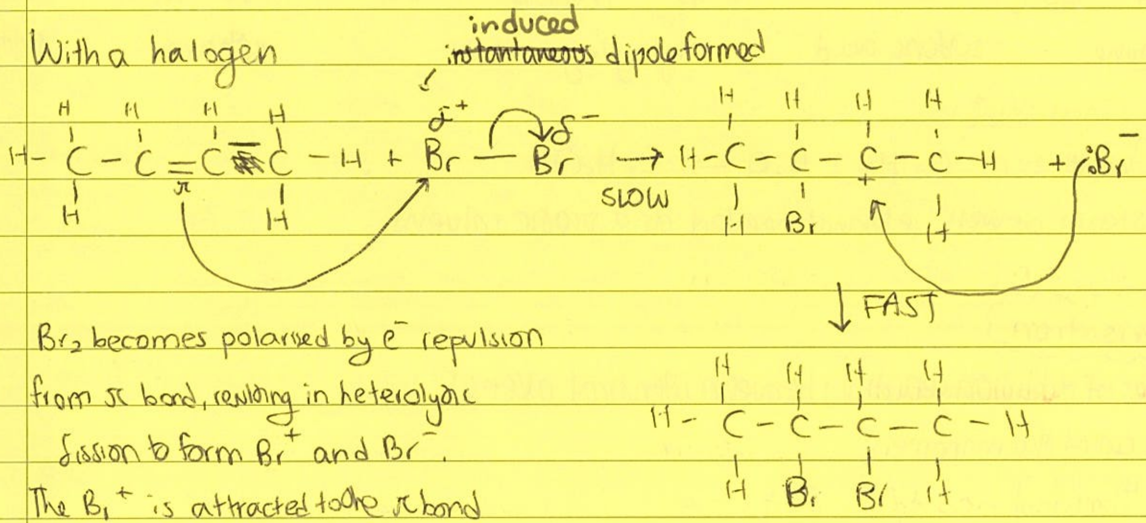
- Electrophile : an electron deficient species that can accept electrons pairs [Lewis Acids]
- Why do alkenes undergo electrophillic ~~additor~~ addition?

① C atoms are sp^2 hybridised, hence trigonal planar shape with 120° bond angles formed. This creates an open structure which makes it easy for electrophiles to attack

② π bond = area of electron density above and below the internuclear axis, hence less associated with the nucleus, ∴ weak and easily broken in addition reactions

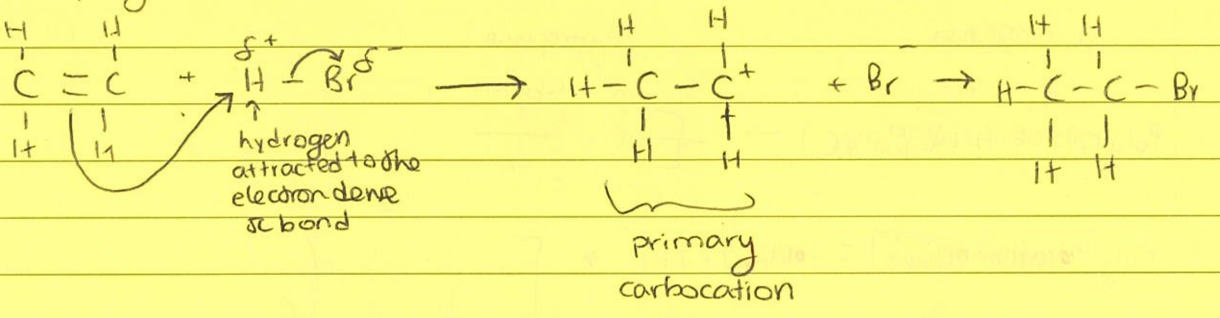
③ Electrons in π bond attract electrophiles

With a halogen



Br_2 becomes polarised by e^- repulsion from π bond, resulting in heterolytic fission to form Br^+ and Br^-.
The Br^+ is attracted to the π bond and attacks it to form a carbocation.
The step is slow and the unstable carbocation reacts with Br^- to form 2,~~2~~3 dibromobutane

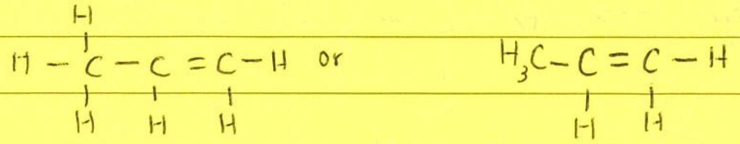
With a hydrogen halide



~~Markinikovs~~ Markovnikov's Rule

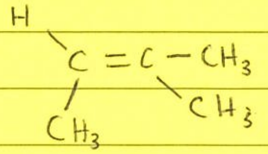
Asymmetric Alkenes

e.g 1)

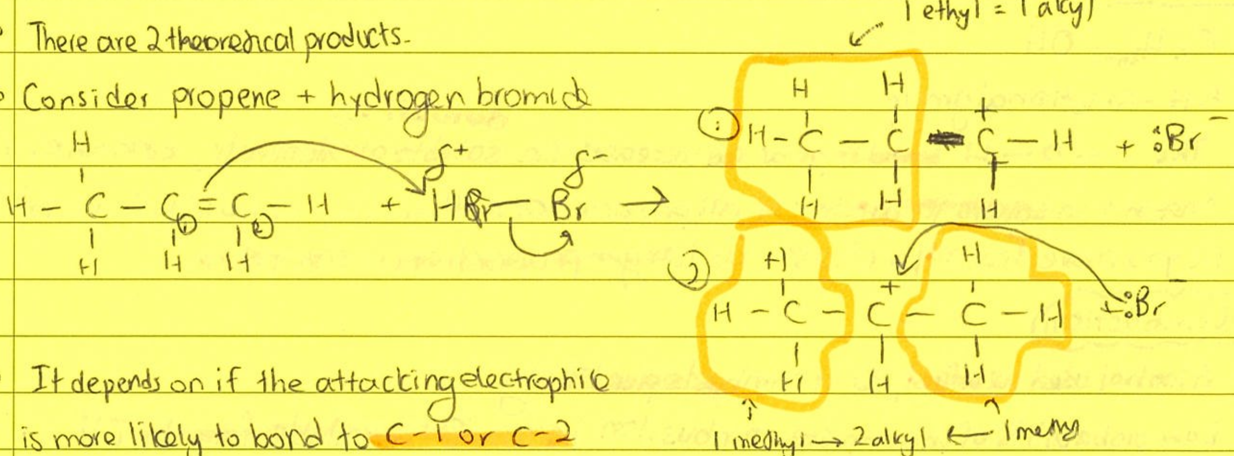


propene

2)



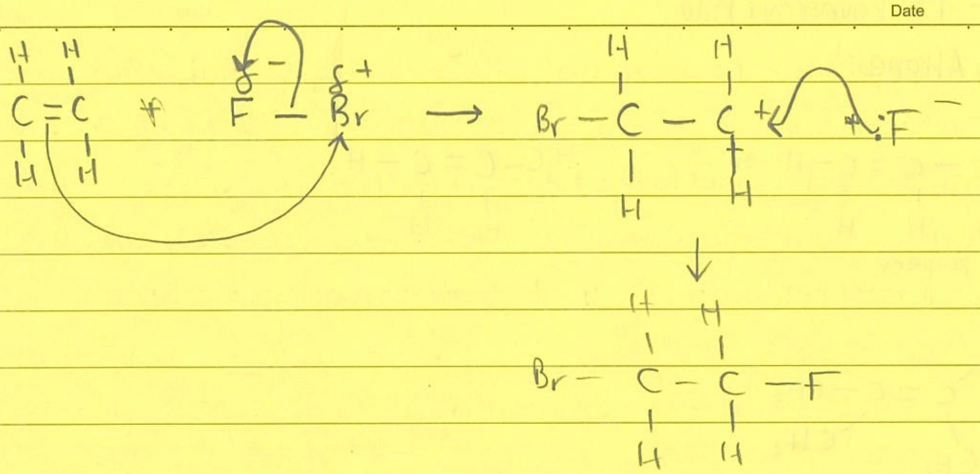
- There are 2 theoretical products.
- Consider propene + hydrogen bromide



- It depends on if the attacking electrophile is more likely to bond to C-1 or C-2
- We look for the most stable carbocation, primary < secondary < tertiary
- More alkyl groups, greater positive inductive effect by moving electrons to stabilise the positive charge ∴ 2 more stable as it is a secondary carbocation, more stable than the primary → this is the major product, due to lower E_a
- Markovnikov's rule states that the H^+ will bond to the carbon with the most hydrogens bonded to it [ergo, the adjacent one will be stabilised by more alkyl groups]
- Formal Definition: The most electropositive atom of the reacting species bonds to least highly substituted carbon atom in the alkene [least ~~alyl~~ alkyl])
- i - inductive effect, e.g double inductive effect
- **Note: write equation in structural form** [$CH_3CH(Br)CH_2$]

Interhalogenic compounds

- $Br^{\delta+}-F^{\delta-}$ → bromofluoride ← because δ^-
- $Br^{\delta+}-I^{\delta-}$ → iodine bromide



Alcohols

- $C_nH_{2n+1}OH$
- OH - functional group
- The — O — H bond is polar and increases the ~~soluble~~ solubility of alcohols, ethanol for instance in soluble in water of all proportions. However, solubility of alcohols decreases as you move down the chain, as larger proportion is non-polar

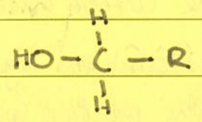
Combustion

- Alcohol used as a fuel, as it combusts plentifully
- Low probability of incomplete combustion because O is available from the OH

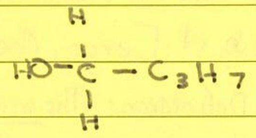
e.g $C_3H_7OH + \frac{9}{2}O_2 \longrightarrow 3CO_2 + 4H_2O$

- ΔH becomes more exothermic ~~due to more~~ as you descend the series as more moles of CO_2 produced

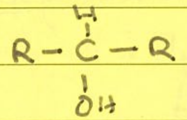
RECALL

Primary Alcohol: 

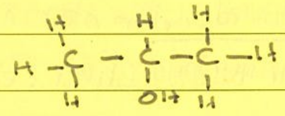
$HO-\overset{H}{\underset{H}{C}}-R$ ⟶ butan-1-ol



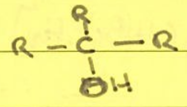
$HO-\overset{H}{\underset{H}{C}}-C_3H_7$

Secondary Alcohol: 

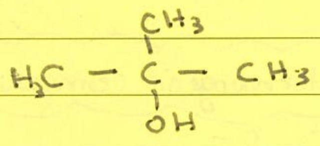
$R-\overset{H}{\underset{OH}{C}}-R$ ⟶ propan-2-ol



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-H$

Tertiary Alcohol : 

$R-\overset{R}{\underset{OH}{C}}-R$ ⟶ 2-methylpropan-2-ol

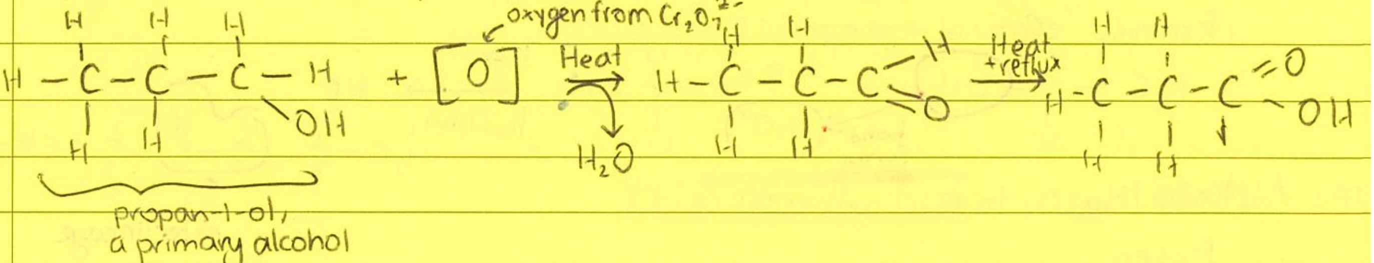


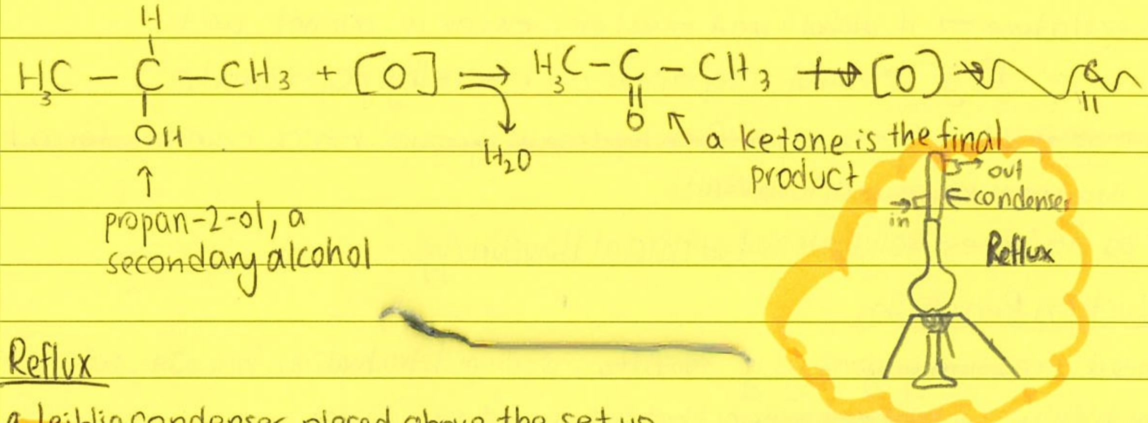
$H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3$

Oxidation

Date No.

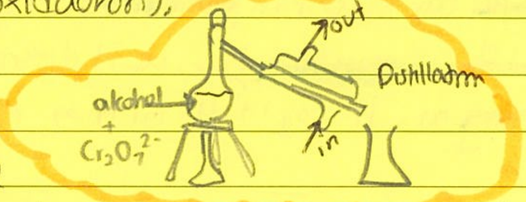
- → Alcohols can be oxidised to aldehydes, ketones or carboxylic acids
- → Tertiary Alcohols cannot be oxidised because of the lack of individual H atoms bonded to the C which is connected to the OH, hence it is difficult for it to be oxidised
- → Need acidified potassium dichromade [VI], which is reduced from Cr^{6+} to Cr^{3+} to gain ~~provide~~ the electrons ~~need~~ produced by the oxidation of the alcohol





Reflux

- → a leiblig condenser placed above the set up
- → ~~Ethanal~~ Aldehydes formed would vapourise due to the loss of ~~a~~ the H-bond, but would condense and fall back down, keeping it in contact with the oxidising agent for a prolonged period of time to increase P (second oxidation).



Distillation

- → We use this if we only want the aldehyde
- → As the aldehyde has a lower b.p than the alcohol, it evaporates, hence they move through a leibig condenser at the adjacent side

Note: The orange to green colour change is only seen if an oxidation occurs, not seen in tertiary alcohols

To test for aldehydes, add Fehling's solution, it oxidises aldehydes to ketones, turning the solution ~~red-brown from blue~~ blue to red-brown

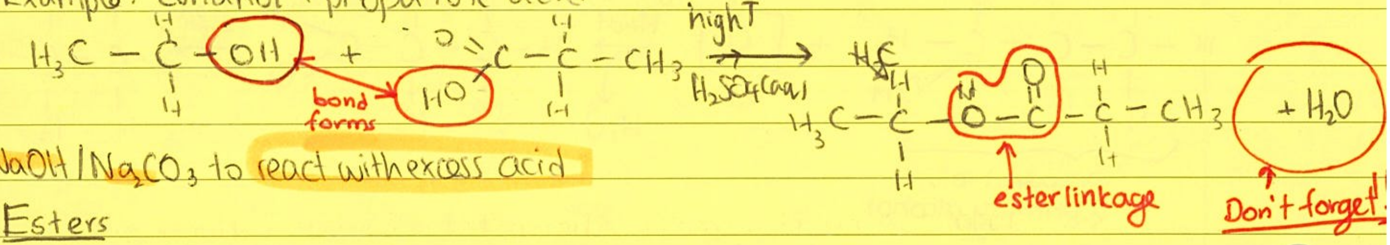
Interestingly, isomers of carboxylic acids are ester.

Esterification

- a condensation reaction between a carboxylic acid and alcohol
- The OHs bond to form an ester linkage and release a H_2O
- It is an equilibrium, hence H_2SO_4 used to shift equilibrium to the right [catalyst]
- esters formed have low m.p and b.p, hence can be seperated by distillation

→ H_2SO_4 used as dehydrating agent to shift equilibrium + lowers E_A ∴ catalyst

Example: ethanol + propanoic acid



IP: Add NaOH / Na_2CO_3 to react with excess acid

Esters

- Nomenclature → if alcohol + acid → ester, ester is alchol, acid
  E.g ethanol + propanoic acid → ethyl propanoate
- Low m.p and b.p because no free hydroxyl groups, hence cannot form H-bonds, and are insoluble in protic solvents
- used as perfumes, solvents and artificial flavouring

Reduction Reactions

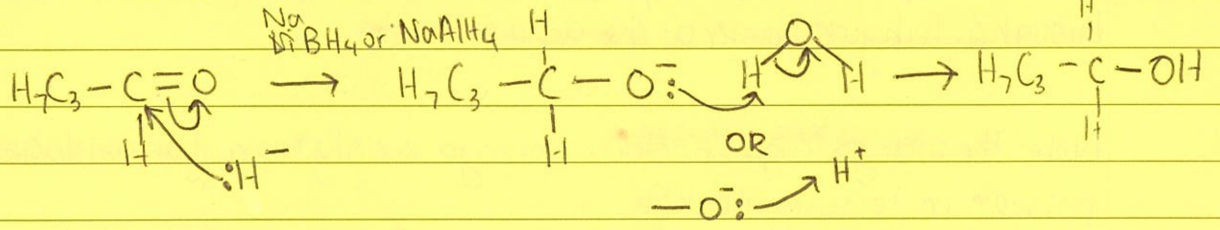
→ We need a reducing agent, e.g $NaBH_4$, sodium tetrahydridoborate, which forms highly unstable H^- ions that act as a reducing agent

→ The H^-s undergo a nucleophillic addition reaction with the electron deficient carbon of a species

→ $NaBH_4$ can be used in protic solvents but cannot reduce carboxylic acids

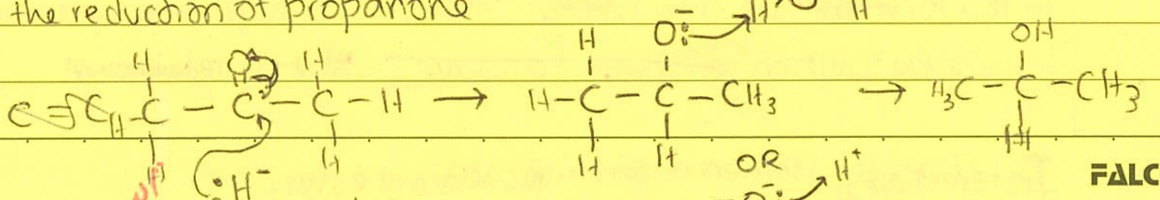
→ Li~~B~~AlH_4 is ~~more~~ stronger, as it dissociates into more H^- ions, but must be kept dry as $H^-(aq) + H_2O(l) \rightarrow OH^-(aq) + H_2(g)$. Hence, only aprotic solvents e.g ethers

→ Consider the reduction of butanal



→ ∴ aldehydes → primary alcohols

→ Consider the reduction of propanone



→ ∴ ketone → secondary alcohol

∴ We can generalise the reductions as follows

~~Keton~~ aldehyde $\xrightarrow[H^+(aq)]{NaBH_4}$ primary alcohol

ketone $\xrightarrow[H^+]{NaBH_4}$ secondary alcohol

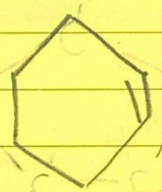
→ Carboxylic acids are more complex, they too are reduced to primary alcohols

carboxylic acids $\xrightarrow[H^+(aq)]{LiAlH_4 \text{ in ether}}$ primary alcohol

Benzene Rings

Cyclic Compounds

→ We have a lot of cyclic compounds in chemistry, such as cyclohexene.



C_6H_{10}

→ Benzene is a prime example, it is an aromatic [has delocalised e^-] unsaturated hydrocarbon.

→ Kekule thought benzene had this structure

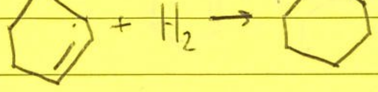
→ In fact, this theory has been falsified because of the 4 pieces of evidence here

for =,
↓ aromat

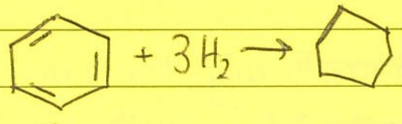
① Low reactivity → with bromine, only bromobenzene, no 1,2 dibromobenzene, unlike what is expected of a compound with 3 double bonds. Dibromobenzene unstable as only 1 positions

② Bond Length → all the C−C ~~bond len~~ and C=C bond lengths were 0.140nm, a value between ~~VS~~ 0.154nm [C−C] and ~~[illegible]~~ 0.134 [C=C], indicating resonance, as it varies the number of electrons in covalent bonds, varying their strengths and therefore, their lengths

③ Enthalpy of hydrogenation



→ $\Delta H = -120 kJ mol^{-1}$



→ $\Delta H = -208 kJ mol^{-1}$

↑ This was expected to be 3(−120), as you need to break 3× as many bonds. It was more stable by about $152 kJ mol^{-1}$!

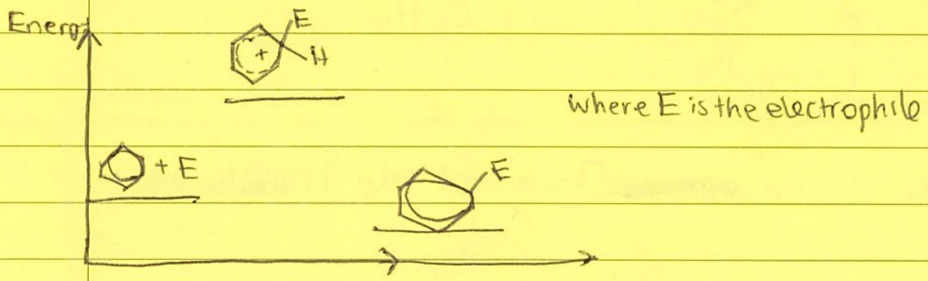
This energy is the amount by which the internal energy of the benzene is reduced. This energy would have to be supplied to overcome the stability of C_6H_6. Hence, it is dubbed resonance energy

④ Isomers → only one isomer exists per compound, e.g 1,2 dibromobenzene
→ 1 isomer for every disubstituted benzene

Note: Addition reactions not favoured because it disrupts the aromatic ring of benzene [cloud / ring of delocalised electron / π bond conjugation]; and resonance energy would be needed. Additionally, the lack of an aromatic ring decreases the stability of benzene. Hence, substitution is prefered, ~~so~~ as they preserve the aromatic ring. Benzene is sp^2 hybridised

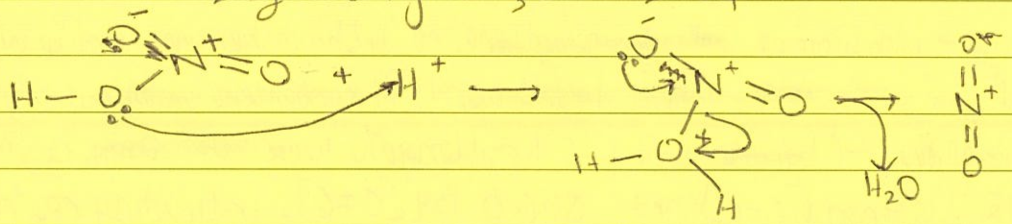
Electrophillic ~~Addition~~ Substitution

→ Benzene is attractive to electrophiles because of its aromatic ring
→ High Ea as the first step disrupts the ~~so~~ π bond conjugation [aromatic ring].

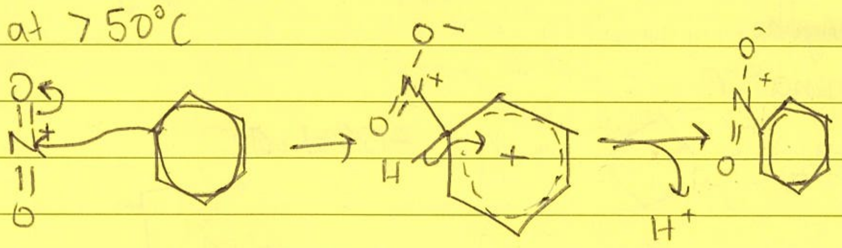


Consider the nitration [add NO_2] of benzene

① We form NO_2 by reacting HNO_3 and H_2SO_4



② NO_2 then is reacted with benzene at no more than 50°C, because further nitration occurs at > 50°C



Be wary of this; ensure the arrow from the H bond goes through the ring, no need to go through C atom.

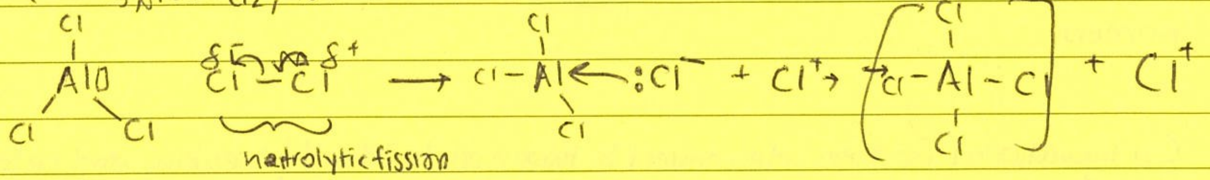
The NO_2^+ ion attacks the p electrons in the aromatic ring, hence an electron is used by the ring to form a covalent bond to the NO_2^+. Simultaneously, the double bond $\overset{+}{N}=O$, splits to $N^+—O^-$. The ~~π bond~~ delocalisation of electrons is now broken and a positive charge is distributed amongst the benzene, forming a carbocation.
A bond to hydrogen is subsequently broken, releasing a proton and the aromatic ring is restored

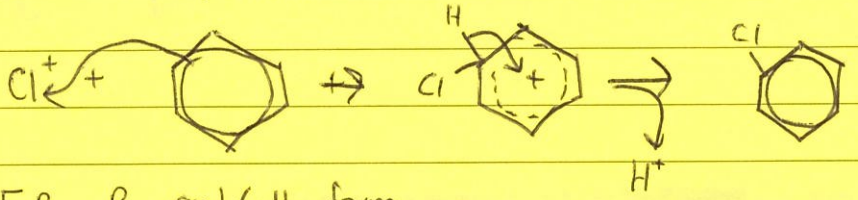
Conditions

① H_2SO_4 - catalyst. H^+ generated can react with hydrogensulfate ion [HSO_4^-] to reform H_2SO_4
② HNO_3 - source of NO_2^+
③ 50°C. ↑ rate, but no higher as it facilitates further nitration

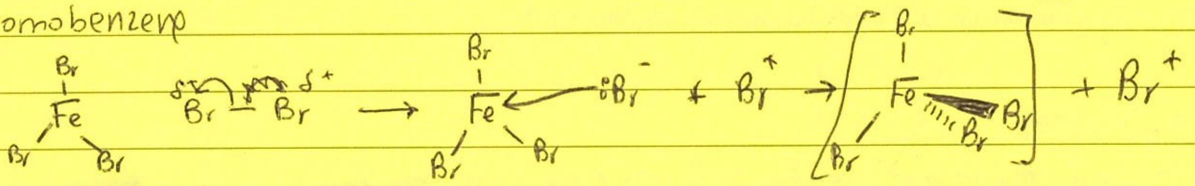
Similar Reaction

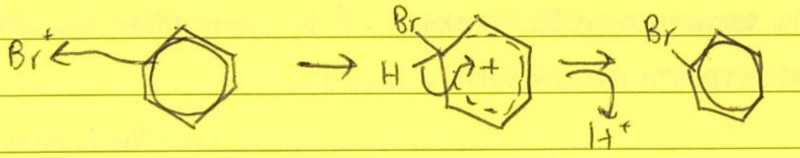
- given $AlCl_3$, and Cl_2, form chlorobenzene





OR, with $FeBr_3$, Br_2 and C_6H_6, form bromobenzene



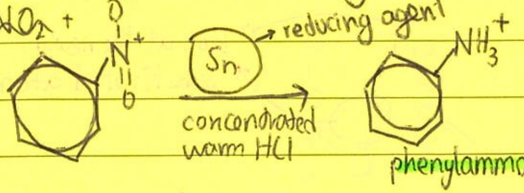


Back to Reduction

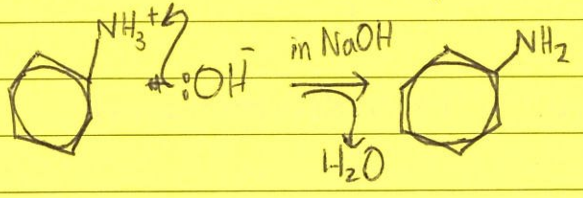
- By a reduction reaction, phenylamine [$C_6H_5NH_2$] can be formed
- $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$

then, under reflux in a boiling water bath

→ ~~$C_6H_5NO_2$ +~~



phenylammonium ion → protonated because of acidic conditions



The NaOH neutralises any remaining $H^+(aq)$.

Overall

~~$C_6H_5NO_2 + 4H^+ \rightarrow C_6H_5NH_2 + 2H_2O$~~

Isomers[Ewww]

Isomers

Structural Isomers
→ molecules with the same molecular formula but different structural isomers

Stereoisomers
→ molecules with the same structural formula but different atom arrangements in space

configurational
→ can only be interconnected[mapping] by breaking a bond
→ Restricted Rotation

E/Z and cis/tran

optical isomers

Configurational isomers interconvert between each other by breaking and reforming a bond

Cis/trans

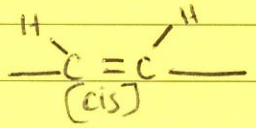
→ exist where there is restricted rotation around atoms

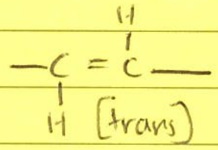
→ e.g always in alkenes because of double bond

We only use cis/ trans for rings systems, otherwise use E/Z or optical

- Alkenes

→ Why?: π + σ bonds make up the C=C bond, the π is formed from an overlap of 2 p orbitals which need to be on the same plane to combine. A bond rotation breaks the π bond, hence there is restricted rotation around atoms, ∴ cis-tran

→ 
(cis)

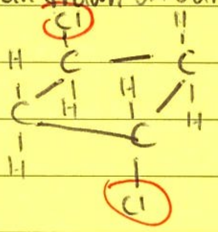

(trans)

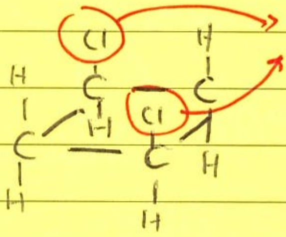
Note: cis alkenes have higher b.ps because of inductive effects on same top/bottom, granting polarity ↑b.p

- Cyclic Compounds [specifically disubstituted ones, e.g 1,2 dichlorocyclohexane]

→ Why?: Rotation restricted because of C-C bonds are part of a ring system

e.g [note, all drawn on same plane]


trans-1,3 dichlorocyclobutane

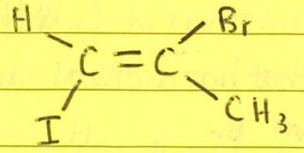

look at the newly substituted atoms

cis-1,3 dichlorobutane

E/Z isomerism

→ like cis/trans, when we have atomic rotational restriction
→ but when C atoms of C=C bonded to more than 2 different molecules

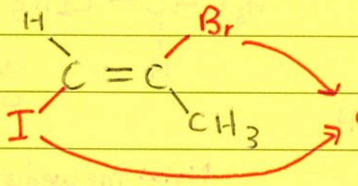
e.g



→ Using the Cahn Ingold Prelog rules of priority, we decide whether we have a E or Z isomer.

① Identify heaviest ATOM bonded to ~~the~~ a side C=C. So it is clearly I for LHS, as Mr(I) > Mr(H) ~~Mr(C) Mr~~ ~~(I) and Mr(H)~~

② Now, check RHS, Mr(Br) > Mr(C), so it is Br



different sides, so it is trans-like ∴ E

- E → reverse of it's cis implication, so trans. 2 diff sides, unlike the 3 bits on the E
- Z → same plane, unlike the 2 bits on the Z

- Z and E are written in brackets. Hence, the example would simply be
  (E)- 1-iodo, 2-bromo pent-1-ene

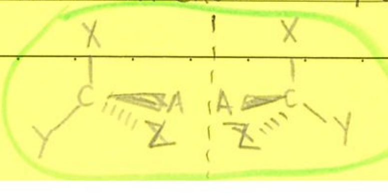
E vs Z

→ different physical properties, e.g b.p, solubility, m.p.
→ different chemical properties as different possible reactions can occur

Optical Isomers

- Enantiomers

→ Definition: isomers that are non superimposable mirror images of one another
→ a chiral carbon is required
→ A chiral carbon is a carbon bonded to 4 different atoms or groups, also called asymmetric
→ 2 enantiomers per optically active molecule
→ We draw them as tetrahedrons, with the chiral carbon at the centre.
→ If asked for both enantiomers, write as the following

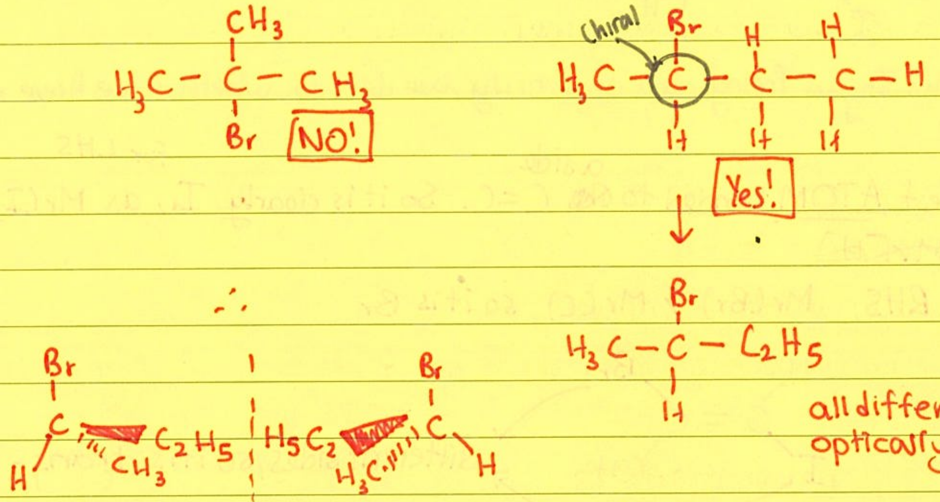


→ a mixture containing a 50-50 mix of each enantiomer is a racemic mixture, and is optically inactive

Rotations in opposite directions with equal magnitudes

→ Identifying chiral carbons. Draw the enantiomers of C_4~~H~~H_9Br

We need an isomer of ~~bu~~ bromobutane that has a chiral carbon

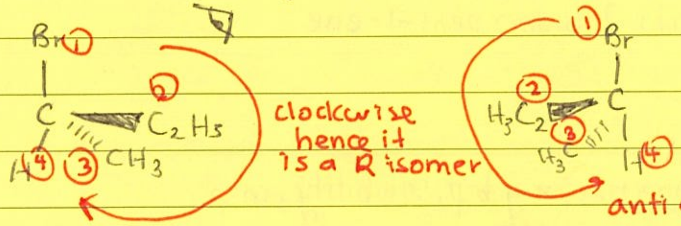


all different groups, hence optically active!

Note: the wedges and dashes must be used!

Something interesting [not in syllabus]

- Distinguishing R and S optical isomers
- Look at the ~~heaviest atom bonded~~ heaviest atoms bonded in order and number them. If 1 → 4 go clockwise, it is R, if anti clockwise then S

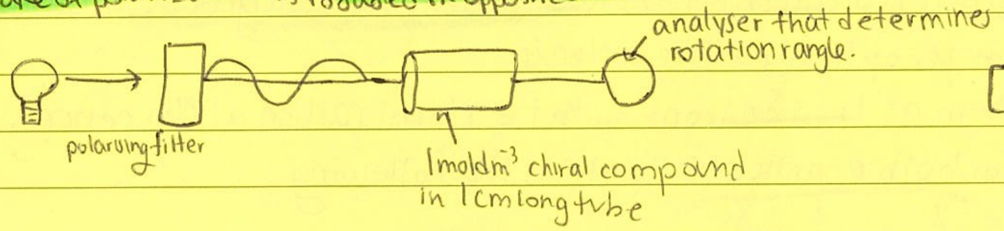


Plane polarised Light

→ a transverse wave~~s~~ of light

→ normal light vibrates ~~on~~ in every plane, but plane polarised light moves perpendicular to the wave. ~~P~~plane Polarised (PP) light generated by shining light through polarising filter

→ Enantiomers rotate plane polarised light, if plane polarised light passed through, the plane of polarization is rotated in opposite direction



[polarimeter]

→ if we have a racemate, there is no net rotation as both chiral compounds rotate clockwise and anti-clockwise, cancelling each other out, ∴ not optically active

→ Note: naturally occuring chiral compounds are optically active, only 1 type of enantiomer

→ clockwise [+ ve angle] is an R isomer, anti is an S

Comparing properties of enantiomers

① Chemical

→ different reactivities, and because biological systems [e.g enzymes] are chiral, it has significant impacts. E.g thalidomide [listen to "We Didn't Start the Fire,"], 1 ~~ch~~ enantiomer reduced morning sickness, another caused birth defects

→ To produce a single enantiomer, asymmetric synthesis is used, a process using a chiral catalyst

② Physical - also differ

Effect

→ Distinct chemical and physical properties allow for seperation

→ Hence, 2 enantiomers in a racemate can be seperated by "resolution."

S_N1 and S_N2 w.r.t stereoisomers

S_N2

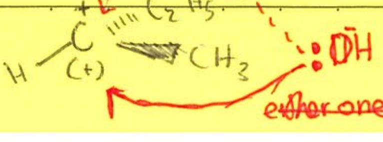
→ it is stereospecific, causes an inversion of spatial arrangement of atoms around a C atom

→ Called stereospecific because the spatial arrangement of atoms in reactants determines 3D configuration of the products

* → This is because bond formation is before bond cleavage in the transition state, ∴ no loss of stereochemistry

S_N1

→ non stereospecific as there are 2 possible bonding sites on carbocation intermediate because it is planar



~~either one possible~~

nucleophile can attack from any position in step 2

→ hence an S_N1 mechanism produces a racemixate, as a mix of optically active isomers are produced.

Question Tips

1) Structure of benzene – C s are sp^2 hybridised, 120° angles, hexagonal, resonance, all equal C-C bonds, bond order of 1.5

Every Organic Reaction

21

Date No.

- Free Radical Substitution

→ UV light

$CH_4 + Cl_2 \rightarrow CH_4 + 2Cl^{\bullet}$ → ~~prop~~ initiation

$CH_4 + Cl^{\bullet} \rightarrow {}^{\bullet}CH_3 + HCl$ → propagation

${}^{\bullet}CH_3 + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$

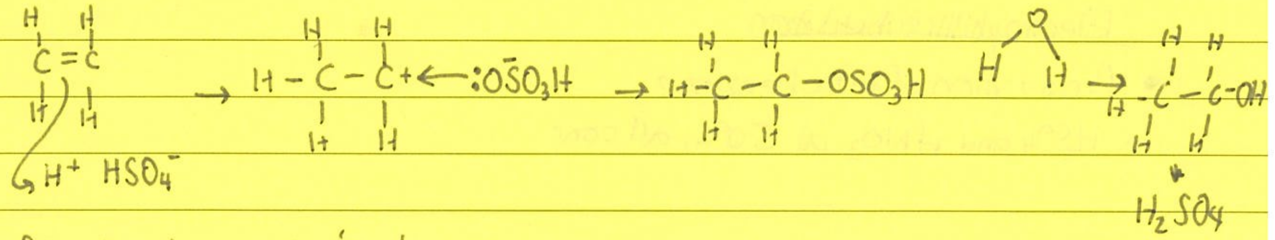
${}^{\bullet}CH_3 + Cl^{\bullet} \rightarrow CH_3Cl$ → termination

Electrophillic Addition

- Hydrogenation → 150°C, Nickel Catalyst, $H_2(g)$

→ alkene to alkane

- Reactions with interhalogeno compounds / halogens [halogenation] / ~~hydrogen~~ halogen halides (hydrohalogenation
- Hydration → H_2SO_4 and H_2O



- Be careful with Markovnikov's rule

Nucleophillic Substitution

- S_N1 if tertiary, S_N2 if primary, both for secondary [protic = S_N1, aprotic = S_N2]
- No conditions
- Convert halo~~gen~~ alkanes into alcohols with a O^-H nucleophile

Alcohol Oxidations

→ All require $K_2Cr_2O_7$ and H_2SO_4, ~~or~~ [acidified potassium dichromate (VI)]

→ alcohol (1°) → aldehyde → carboxylic acid

distillation

reflux

→ alcohol (2°) → ketone

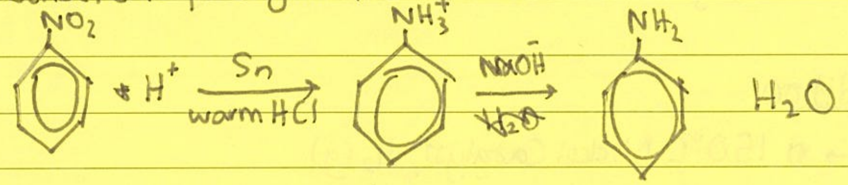
→ alcohol (3°) → no reaction, no Hs to be lost as part of oxidation

Reductions

→ With $LiBH_4$ and H_2O / protic solvent
1) ketone → secondary alcohol
2) ~~primary~~ aldehyde → primary alcohol

→ with $NaAlH_4$ and aprotic solvent (because otherwise H^+ ions gone)
1) carboxylic acid → primary alcohol

→ Nitrobenzene to phenylamine



Esterifications

→ alcohol + carboxylic acid
→ H_2SO_4 catalyst + dehydrating agent [shifts equilibrium]

Electrophillic substitution

- Production of nitrobenzene

→ H_2SO_4 and HNO_3 at 50°C, all conc

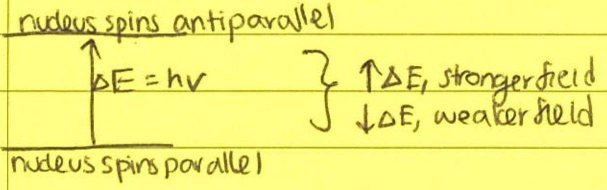
11: Measurement, Data Processing and Analysis

Proton Nuclear Magnetic Resonance Spectroscopy [^{1}H NMR]

→ protons spin, specifically, H' protons

→ When in an external magnetic field, the protons will either spin ~~in~~ in a direction aligned with the field or will spin anti parallel to the field, which requires more energy

→ Hence, 2 energy levels formed

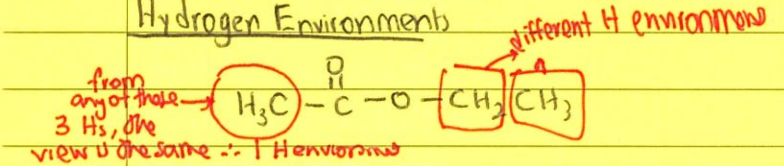


→ Electromagnetic waves are used to excite lower energy protons to the higher level

→ The point in the spectrum where the absorption occurs is called the chemical shift

→ Different chemical environments have different chemical shifts because, for instance, deshielding, when a neighbouring atoms holds the e⁻ in the bond to a greater extent, reduces the shielding from the external magnetic field, ∴ more energy absorbed

Hydrogen Environments

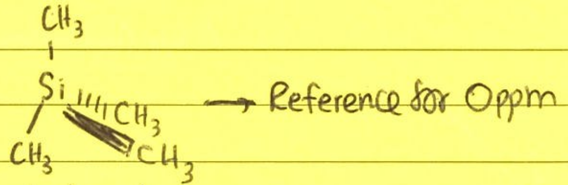


1) Think like a H atom, how many different points are there in terms of perspective?

2) Count up – the number of H environments → number of peaks on a low-res spectrum

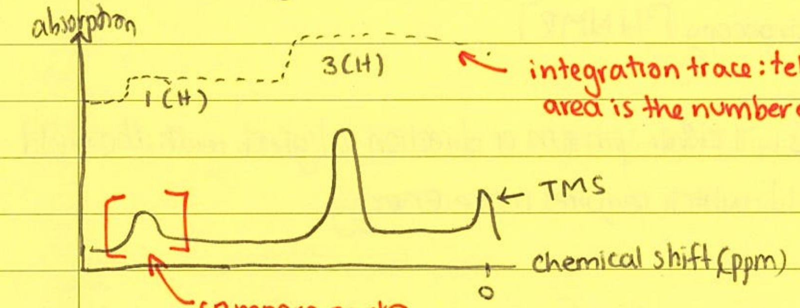
Reference

- tetramethylsilane



- ~~All~~ Single H environment, only 1 peak
- Unreactive, does not interfere with species under study as strong bonds
- Absorption out of range from most other protons
- Low b.p due to LDFs, easy to remove.
- Soluble in most organic molecules

Understanding the spectra

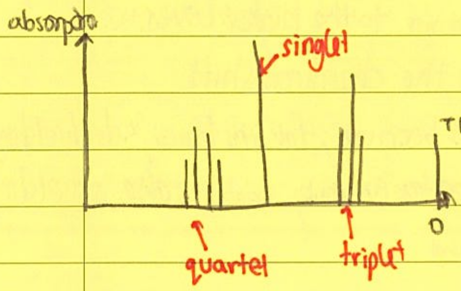


integration trace: tells us the ratio of the areas under the graph, area is the number of H atoms in the $\overset{H}{,}$environment

[Low Res Spectrum]

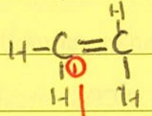
compare peaks and their shift values against data booklet

High Resolution



→ Allows us to determine splitting pattern

→ Splitting = n+1, where n is the number of Hs on an adjacent Carbon.



for 1, 2 Hs on the next C atom, hence 3 splits ∴ triplet

Splitting and Spin-spin Coupling

USES

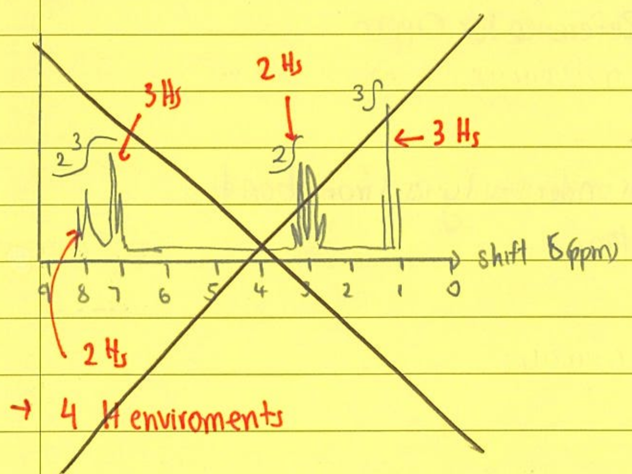
→ Determining structure

→ Medicine → determine extent of damage after heart attacks, check tumours and hydrocephalus

This variant is MRI

Example Analysis

A ~~Low Res Spectrum is shown~~



→ 4 H enviroments

Infa-Red Spectroscopy

→ IR is absorbed by certain bonds, resulting in stretching or bending, giving us information about bonds

→ IR absorption is dependent on a change in dipole moment

→ If ~~expos~~ the new bent or stretched bonds have new dipoles, then those bonds are infared active

→ The seperate δ^+ and δ^-s in a molecule allow the electrical component of IR to increase the vibrational energy of the molecule, producing a corresponding change in the bond's dipole moment. This then affects the polarity of the bond and hence the intensity of absorption

→ Why is HI infared active and I_2 is not? → HI is polar due to the electronegativity difference, hence the electrical component of the IR increases the molecules vibrational energy, resulting in a change in dipole moment and hence an absorption of IR.

I_2 is a pure covalent compound and has no partial charges with which the electrical component of IR can interact with ↓, ∴ infared inactive

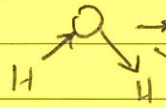
→ Vibrational Frequency and Wavenumber: ↑Atomic Mass, ↑wavenumber, as lower energy, ↑ bond strength, ↑wavenumber, ↑E

Bending and Stretching

1) Symmetric Stretch

→ stretch in same direction in same magnitude, ∴ no change in dipole moment for non polars

2) Assymmetric Stretch



→ stretch in different directions by different amounts

→ Because of unequal lengths, a non-polar has a temporary dipole

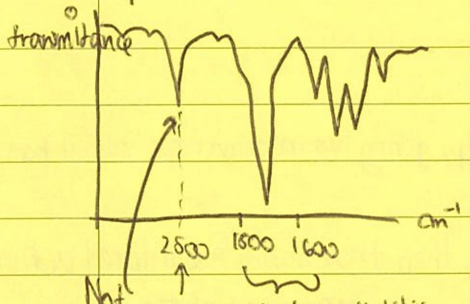
3) Bending → bending away from geometry → produces change in dipole ∴ IR active

Question: What happens on a molecular level when molecules absorb IR

→ The seperate δ^+ and δ^- allow the electrical component of IR to change the vibrational energy of bonds, stretching or bending them. This changes their polarity, and the energy for this is quantised. The polarity then affects IR absorption

NOTE: The finger print region of an IR spectra is 1400-1800, all peaks here distinguish the compounds as a hydrocarbon

Spectra



Not O-H because it is not strong and broad, see data booklet

indicates that it is a C=O → ∴ either aldehyde or ketone

NOTE: Hydrogen bonds → broadened peak as O-H vibration in hydroxyls change, broader absorption + lower frequency

IR can be used to confirm or eliminate potential functional groups, as only IR of certain wavelengths absorbed and other wavelengths transmitted. Functional groups have characteristic IR absorption

Index of Hydrogen Deficiency [IHD]

→ degree of unsaturation

→ number of H_2 molecules needed to fully saturate a molecule [C_xH_{2x+2}]

Formula = $\frac{2x+2-[y]}{2}$, where y is number of Hs

→ Note; halogens = hydrogens ~~and~~ a nitrogen = 1 C and 1 H and O and ~~N~~ S do not affect IHD

Uncertainties and Errors

→ Uncertainty

① Analogue → half of the smallest division

② Digital → the smallest division

③ Unquantifiable → delay in reaction time, point of indicator colour change

Error

① Random → caused by measuring instrument (uncertainties), insufficient data, effect of change in surroundings or misinterpretation of results; reduced by repeats, readings to high balanced by low ones.

② Systematic → poor experimental design / procedure, repeating does not help.
e.g measuring from top and not bottom of meniscus, using a acid base indicator that is clearly unsuitable. We reduce random error by better experimental design.

Accuracy and precision

- Accuracy – how close observed values are to the true value, small systematic error
- Precision : closer to each other, ∴ low random error and reproducible.

Percentage ~~Error~~ Uncertainty and Error

Uncertainty

$\frac{|\text{uncertainty}|}{\text{measured value}} \times 100\%$ ⟶ Add all % uncertainties up, this = total random error

Error (Total)

Absolute uncertainty = calc value × % uncertaint

$\frac{\text{True value} - \text{experimental value}}{\text{true value}} \times 100\%$

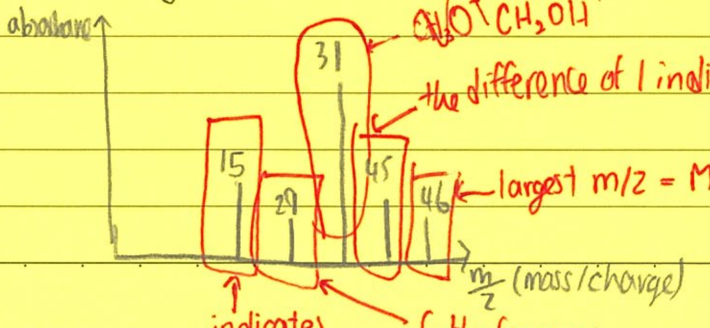
Rounding off answers

- If adding or subtracting → use the d.p given, not s.f e.g $5.00g - 2.83g = 2.17g$ (2.d
- If multiplying or dividing, use s.f of least precise apparatus.

E.g heat ~~prod~~ needed when 0.125kg water heated to 35°C from RTP = $q = mc\Delta T = 0.125kg \cdot 4.18 \times 10$
$= 5.225 ∴ 5.2kJ$ (2 s.f)

Mass Spectrometry

- determines Mr of a compound
- Molecule is ionised as followed → $X_{(g)} + e^- \rightarrow X^+_{(g)} + 2e^-$, same RMM, corresponds to the largest peak. This $X^+_{(g)}$ ion is called the parent ion
- However, one ~~ion~~ molecule can be further fragmented, to form different ions that are detected by the mass spectrometer
- Using the fragmentation pattern, we can deduce structure.



~~CH_3O^+~~ CH_2OH^+

the difference of 1 indicates loss of H → also mass of $C_2H_5O^+$

largest m/z = M_r of $X^+_{(g)}$ = Mr of X = 46

indicates a CH_3^+ fragment

C_2H_5 fragment

C_2H_5OH has Mr = 46, and free CH_3 indicates methyl, C_2H_5 indicates ethyl.

H H
H−C−C−O−H

When comparing frag patterns, compare why one has a particular peak while another does not, compare overall Mr and any implicit functional groups. Compare peaks, one peak would be larger because of more sites for fragmentation.

Waves

Radiowaves - used in HNMR, to be absorbed by nuclei, allow spin reversal
Microwaves - used to increase bond rotational energy → for bondlength
IR - stretch / bend bonds in IR spectrometry
(UV) / VL - produce electronic transitions → e.g Lyman series for H emission spectra
X-Rays - When electrons make transitions between inner energy levels → produce diffraction patterns.

Option D: Medicinal Chemistry

Semantics

Date No.

- → Drug: a chemical that affects how the body works [good and bad effects]
- → Medicine: a chemical that improves health
- → Both of them do the following → ① Alters physiological state [consciousness / activity level / coordination] ② Alters incoming sensory information ③ Alters mood, emotion

Administration

① Oral → pills, liquids
② Inhalation → nicotine (vapour form)
③ Rectal → suppositories
④ Parenteral → injections

Parenteral

- → Intravenous → deposited directly into bloodstream, for ~~vaccin~~ local anaesthetics
- → Intramuscular → injected into muscle, for vaccines
- → Subcutaneous → just under skin, into adipose tissue [subcutaneous tissue], for dental injections

Bioavailability

Def: Fraction of administered dosage that reaches the target part of the body

- → hence drugs administered by intravenous parenterals have 100% Bioavailability and are used as a metric for comparison
- → Very important as it determines dosage

First Pass Effect

- → When medicine administered orally, not all will enter the bloodstream because in the digestive system, enzymes act as biological catalysts, breaking down the drug in the stomach, liver or small intestine. The liver is the site of further metabolic breakdown

Factors affecting Bioavailability

① Administration: intravenous avoids first pass effect; morphine administered intravenously because low bioavailability of 30% when administered orally because the remainder is ~~administered~~ metabolised by the liver

② Polarity: Non-polar, lipid soluble drugs are more effective at ~~enterin~~ passing through the phospholipid bilayers in the brain. However, polar drugs can dissolve in the aqueous blood plasma. Take heroin as an example, has less polar ester groups that crosses blood-brain barrier effectively, unlike morphine, which has polar hydroxyl groups

③ Functional groups: Acid/Base groups can determine charge on drugs at different pH values and hence affect its reactivity and solubility. Look at pK_a and pK_b

Drug Action

- → dependent on interactions with receptors, enzymes, fibrous proteins in the p.l bilayer. The binding prevents or disrupts biological activity → interrupts disease
- → The greater the chemical fit between the drug and the receptor, the greater the drug activity
- → forms supramolecular complexes by LDFs, H-bonding or ionic bonding

Physiological Effects

① Therapeutic - beneficial, either intentional or not

② Adverse - harmful outcome, intentional or not

③ Side effects → non-intended physiological effects that can be positive or negative

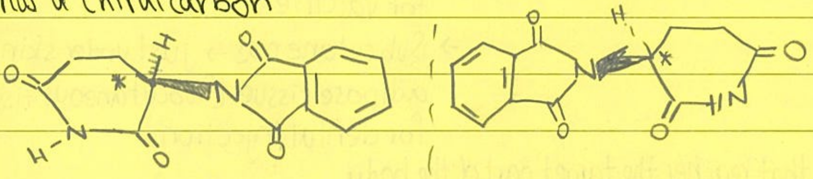
Example - diphenhydramine

Therapeutic → dries mucous membranes } swapped when treating insomnia

Side Effect → drowsiness

~~Shadow of Thalidomide~~ Children of Thalidomide

Recall: Optical isomerism is when a compound can exist as 2 non-superimposable mirror images or has a chiral carbon



→ The enantiomer used to combat morning sickness was non mutagenic but because it was sold as a racemate, R and S variants were present, the S was teratogenic, inducing severe deformities in the fetus

Tolerance and Addiction

→ Tolerance: reduced response to drug of same dose → Why? Body becomes more efficient at metabolising the drug [↓ bioavailability], drug receptors become less effective. Hence, increased doses are required for a therapeutic effect → dangerous, as approaches toxic dose levels

→ Addiction: ask Sugi. ~~Neede~~ Patient becomes dependent on the drug to stay normal and suffers withdrawal symptoms if not taken. Minor for caffiene (headaches) but serious for opiates, alcohol and barbituates

Therapeutic Index (TI)

→ used in reference to dosing regime → which aims to maintain constant level of [drug]. We need to keep the [drug] ~~is~~ within safe levels but enough to induce therapeutic physiological effects

→ The therapeutic window is the range of doses between the minimum amounts of the drug to produce the desired effect and medicinally unacceptable adverse effects.

→ Quantified as TI

→ ED_{50} → minimum effective dose that produces the therapeutic effect in 50% of the population

→ LD_{50} → dose that is lethal to 50% of population

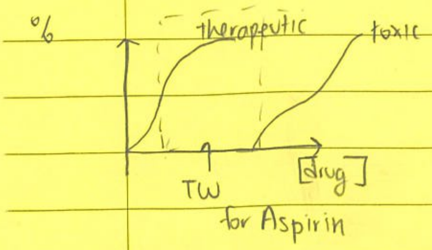
→ TD_{50} → dose that is toxic to 50% of the population

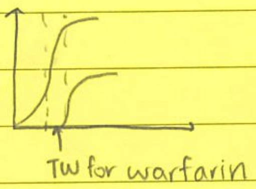
$TI\ (\text{animals}) = \frac{LD_{50}}{ED_{50}}$

$TI\ (\text{humans}) = \frac{TD_{50}}{ED_{50}}$ (not ethical to kill humans)

Danger of a Low TI

→ e.g warfarin → lower margin between toxic and effective doses, correct dosage is crucial, not safe if taken in slightly higher doses





Things to account for with dosage

1) Sex
2) Age
3) weight
4) Diet
5) Environment
6) Side Effects, tolerance, addiction

→ hence blood plasma concentrations must be monitored

Development of Drugs

① Identifying Needs → it is a major investment, hence industry is selective in focus, ∴ lots into cardiovascular disease, obesity and cancer. Context: control of licensing of drugs – average dev time from identification → market is 10–12 years. Less focus on serendipity, use of rational drug design [identifying molecular target and designing drug to interact].

② Identify a compound → called a lead compound, used to start design of drug. Usually from plants e.g lead compound from yew trees lead to Taxol. Analogues now created (chemically related compound) Done using combinatorial chemistry → produces and tests many potential medicines

③ Testing → Animals first ~~the humans~~ → ethics and safety say this should be minimised. From here, therapeutic index calculated

④ Human Testing → Phase I: 50-100, Phase II: 200-400, Phase III 3000+, them with placebo to provide basis for comparison

For the drug, need to also find structure, possible synthesis, extraction and yield

D2 → Aspirin and Penicillin

Analgesics

→ Painkillers, interfere with transmission of pain signals

→ Strong: Only available on prescription, interact with receptors in brain that reduce the transmission of pain signals in the brain and spinal cord. They bind to receptor sites of neurons, hence preventing the chemical neurotransmitter that has passed through the synapse from binding to a new neuron. Target Organ = Brain. E.g heroin, morphine

→ Mild/Weak: intercept pain stimulus at the source. Hence, target organ is the site of pain. They act as a competitive inhibitors and bind to the active side of prostaglandin synthase, interfering with the production of prostaglandins, which transmit pain signals to the brain + causes fever + swelling

Aspirin

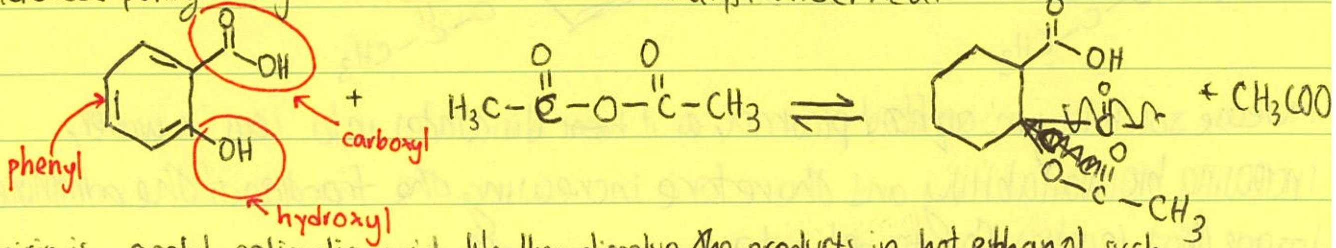
~~Prop~~ Medical Profile

Therapeutic Effects: → also antipyretic prophylactic [preventative] blood thinner (anti coagulent) to prevent strokes or heart attacks. Because it blocks productions of prostaglandins, it is a mild analgesic.

Side Effect: Bleeding in stomach lining [amplified by synergistic effect of taking alcohol with aspirin]. Due to carboxyl functional group, can cause acidosis (↓ blood pH)

Preparation

① salicylic acid is reacted with ethanoic anhydride (condensation of 2 CH_3COOHs) to provide increased purity + higher rate with an acid catalyst under heat

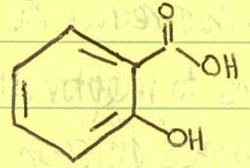


② *Aspirin is acetyl-salicyclic acid. We then dissolve the products in hot ethanol, such that aspirin dissolves but impurities do not, allowing asprin to recrystallise, increasing yield and purity. Cold water is then used to prevent complete dissolution in ethanol

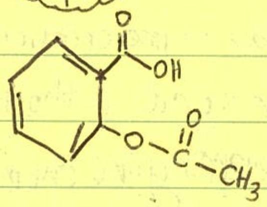
Characterisation by IR

Note

Salicyclic Acid



Aspirin



Similarities

1) carboxyl group ∴ broad absorption for $2500_{cm^{-1}} \leq x \leq 3500 cm^{-1}$

2) Ester group → each registers <u>at least 1</u> C=O

3) C-H bonding for $500_{cm^{-1}}$ - $1800 cm^{-1}$

Differences

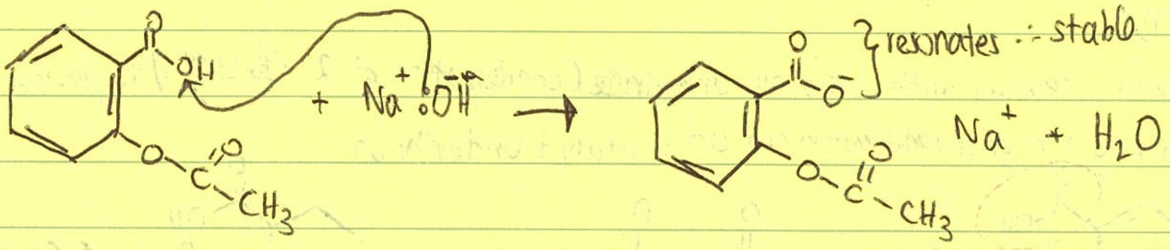
1) 2 C=O peaks for Aspirin, as 2 C=Os, 1 higher in cm^{-1}, because of increased polarity

2) No alcohol ~~C~~-O-H absorption

Testing

→ use m.p, aspirin is 138-140°C. Impurities ↓ m.p + cause wider range

Increasing Solubility



- increase solubility in aq blood plasma, as it ~~beeor~~ dissociates into ions in water, increasing bioavailability and therefore increasing the fraction of the administered dosage that reaches the target site, hence more effective
- Once in ~~the~~ a strongly acidic environment, it reverts to its unionised form (e.g stomach)

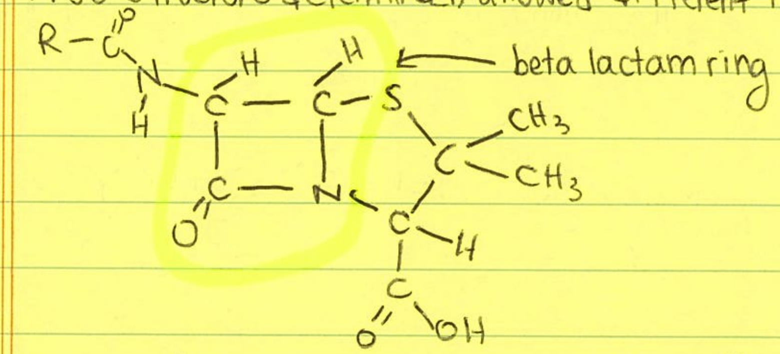
Synergistic Effect with Alcohol

Penicillin

→ Serendipity at play; Alexander Fleming discovered an area on a bacteria sample that was left bare, near a fungi that had grown.

→ Penicillin G [original] was produced by penicillinium notatum (fungi)

→ 1950 structure determined, allowed different types to be produced.



→ Normally, the ring would ~~be~~ have angles of 109.5° due to the sp^3 hybridisation of the atoms but has 90° angles due to restrictions. It is naturally produced, no chemical explanation as to why as of now.

Strained structure

→ Makes carboxyamide group highly reactive, can cause ring to open.

→ Bacteria require a cell wall to prevent ~~pr~~ bursting and prevent entry of unwanted substances, they use the enzyme transpeptidase to maintain their cell walls [cross-linkages]

→ The B-lactam ring breaks in contact with it and acts as a competitive inhibitor, blocking the action of the enzyme

→ ∴ cell wall production fails due to preventing cross-linking

→ Water floods in due to Δ osmolarity (concentration of osmotically active solutes), leading to bursting

Resistance to Penicillins

→ some bacteria, by natural selection, develop genes that code for the production of B-lactamase or penicillinase as it is known colloquially.

Reasons – ① Overprescription → lead to increased number of bacteria exposed to penicillin, more mutations per unit time, leading to greater proportion developing resistance genes. ② Patient Compliance

→ modify side chain to reduce the ability of B-lactamase to break the B-lactam ring before contact with transpeptidase, e.g a phenyl group [additional]

D.3 : Opiates

Opiates

- narcotic analgesics derived from the opium poppy
- directly interfere with brain (interfere with transmission of pain impulses in the brain's relay neurons)
- bind to opoid receptors located at the synaptic cleft on both pre and post synaptic neurones
- blocks transmission of pain impulses between brain cells
- ergo, ~~it~~ strong analgesics such as opiates interfere with the perception of pain without depressing the central nervous system
- only available on prescription, given to relieve pain from serious injuries or disease (heart attacks, cancer e.

Side Effects

Short Term

- ~~Europhia~~ Euphoria
- Dulling of pain
- Depress nervous system
- slower breathing + heart rate
- inhibit cough reflex (why Jane from Breaking Bad died)
- ~~nae~~ nausea + death

Long Term

- Constipation
- Disrupt menstrual cycle
- Addiction
- Social problems
- ↑ risk of HIV/AIDS

The Blood brain barrier

→ brain surrounded by a non-polar ~~ph~~ membrane

→ protects brain by restricting entry of substances that can enter from the blood (e.g pathogens)

→ Lipid based, hence non-polar

→ polar molecules have limited capacity to diffuse across

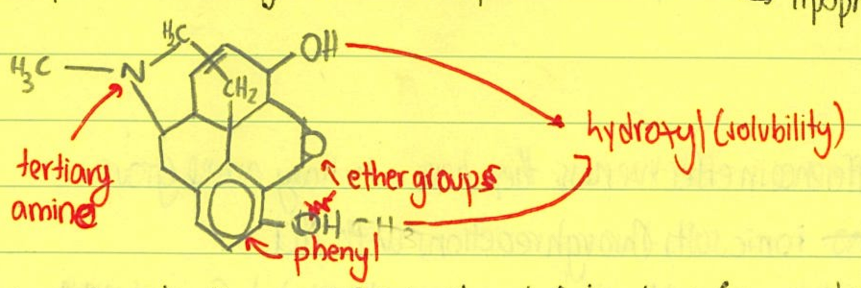
→ Drug must be non-polar and lipid soluble to easily pass through

→ but solubility in water is still important → transported by blood to the brain

→ lipophillic molecules pass through best

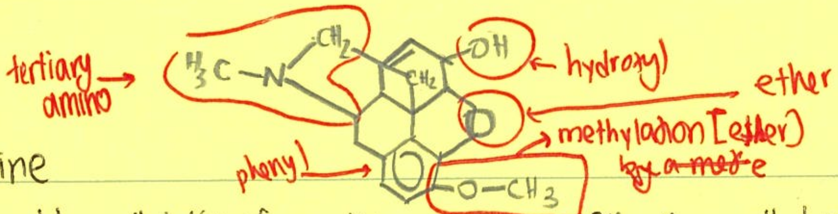
Specific Opiates

① Morphine → naturally found in raw opium



→ in cough medication and ST treatment of diarrhoea (as opoid receptors are associated with contractions of smooth muscle in the gastrointestinal tract)

→ used to produce heroin and codeine through semi-synthetic routes



Codeine

- produced by methylation of morphine, replaces an OH with a methyl ~~ester~~ ether
- less polar, can cross BBB better
- drop in binding capacity to opoid receptors, weaker analgesic than morphine
- Codeine's active metabolite is morphine (broken down into morphine by metabolic reactions) (CYP2D6)
- This metabolic reaction is glucuronidation

3) Diamorphine [Heroin]

→ produced by an esterification reaction with morphine, replacing both OHs with ester groups

→ reagent: ethanoic anhydride or ethanoic acid

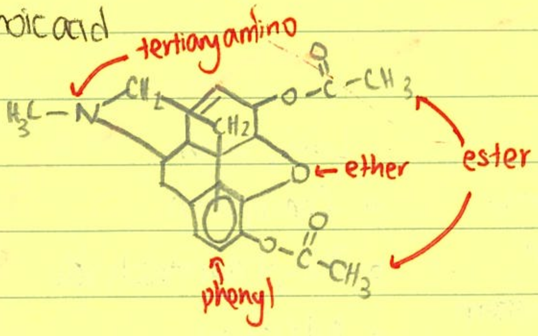
→ decrease polarity significantly

→ can cross BBB more efficiently

→ Context: brain is target organ

→ greater binding to opoid receptors per unit time

→ reaches brain faster and in higher concentrations



Interesting: 6-acetylmorphine more potent than heroin, not hydrolyzed by esterases

NOTE: Codeine and Diamorphine are semisynthetic drugs, (obtained by a synthetic reaction to a naturally occuring compound). They are prodrugs, meaning their metabolites, mainly morphine, are the compounds that bind to opoid receptors. E.g heroin broken down by esterases. Administered via intravenous parenteral

Heroin v Morphine

- apart from the previously explained difference in effectiveness, they have a tertiary amine group
- allows conversion into ~~tertiary amino~~ ionic salts through reactions with HCl
- Heroin can be administered as diamorphine hydrochloride, reverts to undissociated form at BBB
- ↑ Bioavailability

Advantages and Disadvantages

WHO Pain treatment assignment

① Pain Persisting or increasing - mild analgesic (e.g aspirin)
② Greater pain persisting or increasing - use weak opoid (e.g codeine)
③ Complete pain relief - strong opoid e.g morphine

Intravenous morphine is most commonly used in cases of severe pain.

Disadvantages (see first page of D3 for more)

① Addiction → dependence on drug to ~~rem~~ maintain a normal psychological and physiological state
Withdrawal symptoms (e.g cold sweats, anxiety, cramps) may manifest if the drug is not taken regularly. Compounded by increasing tolerance, ~~more~~ higher doses to bring about therapeutic effect, more exposure. Leads to (apparently, in most cases, this is an acceptable answer) thieving, prostitution and ~~drug~~ other crimes

Treating Addiction → slow + difficult. Using an alternative analgesic such as methadone works. Reduces craving and halt withdrawal symptoms → but does not produce euphoria

D4 : pH regulation of the stomach

D4 : pH Regulation in the Stomach

Active Metabolites

- active forms of a drug after it has been metabolised (processed by body)
- The effect of the active metabolite may be stronger than the drug, e.g morphine is the active metabolite of codeine.
- ∴ may be responsible for therapeutic effects

The Stomach

→ low pH (1-2) as this is the optimum for pepsin, an exopepsidase in the stomach that breaks down polypeptides into dipeptides
→ HCl secreted by parietal cells in gastric glands within the stomach lining
→ Aside from establishing optimum conditions, kills any pathogens that enter

{Excess Acidity}

- may be caused by the following factors
  → excess alcohol
  → stress
  → drugs
  → microorganisms e.g heliobactor pylori, which results in ulcer formation by burrowing into mucus lining, (inflammation)
- Results in the following
  → discomfort in stomach (dyspepsia)
  → heartburn
  → acid reflux
  → ulceration
- eats away at mucus lining

H-2 Receptor Antagonists

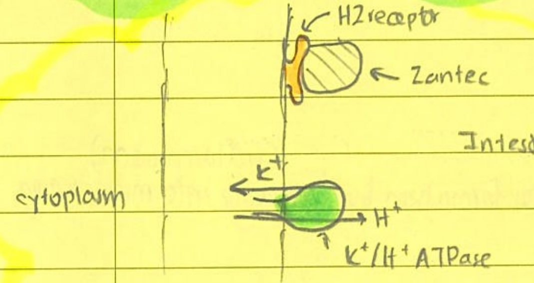
- histamines are produced by enterochromaffin-like cells (ECL cells)
- bind to H-2 receptors on the membranes of parietal cells, stimulating the release of acid
- H-2 receptor antagonists (e.g ranitidine, a.k.a Zantec) bind to the H-2 receptor and block histamine binding, thus preventing / reducing the release of HCl from parietal cells, inhibiting H^+ production
- The data booklet has this molecule's structure
- Developed from histamine analogues, over the counter drug as well

Side Effects

→ diarrhoea
→ headaches
→ dizziness

Proton Pump Inhibitors (PPIs)

- Gastric H^+ secretion involves the use of the K^+/H^+ ATPase proton pump
- Uses energy from ATP hydrolysis to use active transport to bring K^+ from ~~instes~~ intestinal lumen into cytoplasm. The energy released by ATP hydrolysis is also used to actively transport H^+ from the cytoplasm into the intestinal lumen
- Ensures electrochemical neutrality
- inhibits acid secretion
- Omeprazole (Prilosec) and esomeprazole (Nexium), both competitive inhibitors of K^+/H^+ ATPase
- Nexium is ~~a~~ an enantiomer of prilosec
- Prilosec is a racemate and ~~shifts~~ undergoes a chiral shift (on Sulfur) into active enantiomer
- Hence, prilosec's active metabolite is Nexium.



A diagram showing a cross-section of a parietal cell membrane

Antacids

→ neutralise acid directly (non specific reactions)
→ weak bases
→ Cannot use strong as they are caustic and could harm the stomach
→ ~~prevent acid from attacking~~ damaged/exposed stomach lining
→ allow ulcers to heal
→ e.g milk of magnesia ($Mg(OH)_2$ and MgO) milk because of white precipitate.
→ Recall acid-base neutralisation reactions
→ Al slower dissolving, longer effect, constipation
→ Mg fast acting, laxative

Syllabus Stated Antacids

1) $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$
2) $Ca(OH)_2(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$
3) $Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$
4) $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$
5) $NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

Side Effects

PPIs and H2 Antagonists

→ diarrhoea, headaches, dizziness
→ ↑ risk of osteoporosis + allergy dev

Antacids

→ Al linked to Alzheimers
→ flatulence + stomach bloating [$CO_2(g)$]
→ Alter absorption of other drugs

Buffers

~~Ka~~ For $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$

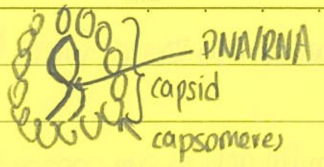
$K_a = \frac{[H_3O^+][A^-]}{[HA]}$, we assume [HA] initial = [HA] equilibrium, $[H_2O]$ same ~~and~~

$pH = pK_a - \log_{10}\left(\frac{[acid]}{[salt]}\right)$

SEE CHAPTER 8 NOTES

D5: Antiviral Medications

Viruses



- → sub microscopic pathogens
- → not classified as living organisms, lack a metabolism
- → only reproduce in host cell, take over metabolism by carrying genes into cytoplasm
- → Host cells assemble viral components using ribosomes, when the host dies, these new viruses are released into the fluid environment of the organism

Bacteria	v	Viruses
→ complex prokaryotes		→ simple, lack structures for medabolism
→ specific bacterial processes e.g building up cell wall, can be blocked by antibiotics		→ no structures/processes for antibiotics to target (v. little targets for drugs)
→ reproduce by binary fission		→ reproduce using host cell, DNA/RNA replication
→ cell membrane and cell wall		→ protein coat, no cell wall or membrane (capsomeres are constituent proteins)

Why are viruses a big problem?

- → mutate quickly, different antigens, no secondary immune response by memory cells.
- → May lay dormant, and the mutated form may cause a flare up
- → e.g Chicken pox, herpes, HIV/AIDS
- → lie in host cells, no significant change to antigens, so difficult to target cells
- → Divide and spread rapidly → begets more mutations per unit time
- → Render vaccines mute to an extent, new mutations ∴ different antigens [see Biology 11.1 Notes]

Antivirals

① Alter cells genetic material so the virus cannot insert its own genes in

② Block enzyme activity in the host cell, so virus cannot multiply or leave

Oseltamivir (Tamiflu)

- → acts as a competitive inhibitor on neuroaminidase, an antigen enzyme on the influenza virus
- → CONTEXT (for non-biologists): Neuroaminidase is an enzyme on the influenza virus that catalyses the degredation of linkages between a virus and the cell that has released it. It's reverse, hemagglutinin, is another glycoprotein that enables docking. Neuroaminidase catalyses a cleavage reaction that allow new virus particles to escape. Snips of a sugar molecule or glycoprotein link to the phospholipid bilayer.

→ influenza has several forms that may or may not have the same antigens → not a universal fix!

→ Tamiflu acts as a competitive inhibitor that binds to neuroaminidase's active site

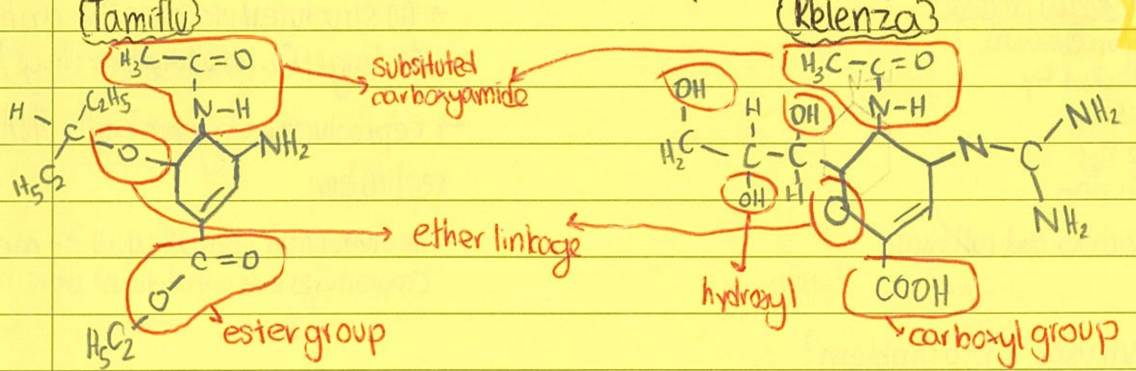
→ Inhibits breakdown of the links, hence prevent release of new viral particles

→ This is a prophylactic ~~d~~treatment

→ Relenza acts in the same way, both have similar structure to sialic acid.

→ Tamiflu is hydrolysed to its carboxylate anion, which is its active metabolite

Comparing the structures of Tamiflu and Relenza



→ oral administration	→ inhalation
→ resistance observed	→ no observed resistance YET
→ nausea, vomiting	→ possible asthma

HIV and AIDs

→ human immunodeficiency virus and acquired immuno deficiency syndrome

→ AIDs is a syndrome, characterised by a very weak immune system → succumb to diseases like pneumonia

→ HIV ~~to~~ antigens bind to receptors on $CD4^+$ ~~B~~T lymphocytes, allowing it to penetrate the cell

→ Retrovirus, has RNA, which it converts into cDNA in the cell by reverse transcriptase. Integrates cDNA into the cell's genome

Why is HIV so difficult to treat?

① Attacks helper-T lymphocytes, hence can no longer activate B lymphocytes to stimulate immunoresponse
② Rapid accumulation of mutations - variations mean memory cells no longer effective
③ Virus lies dormant - difficult for immune system to detect
④ Easily transmitted - body fluids, needles, via placenta

Antiretroviral Drugs

- interrupt stages of HIV life cycle

① Virus antigens bind to receptors on the CD4+ T-lymphocyte's plasma membrane

Possible Treatment: Antagonist molecule could be introduced to block binding, stop virus docking

② Virus enters host cell by endocytosis

Possible Treatment: Alter cell membrane's fluidity

③ Virus loses protective coat and releases reverse transcriptase and RNA, the former converts RNA → cDNA

Possible Treatment: Drugs that stop loss of capsid. More effective: AZT, a competitive inhibitor of reverse transcriptase. As only retroviruses use reverse transcriptase, does not affect normal cells. Stops integration of virus DNA into the cell's genome

④ New viral RNA and proteins synthesised

Possible Treatment: Alter genome to inhibit production

⑤ Virus particles exit the cell

Possible Treatment: Use drugs that prevent exit, e.g Oseltamivir's action as a competitive inhibitor on neuroaminidase

Date No.

D6: Environmental Impacts

{Nuclear Waste}

→ produced from nuclear medicine

→ High Level Waste: gives off large amounts of ionising radiation over a long period of time (high $t_{\frac{1}{2}}$)

→ Low Level Waste: gives off small amounts of ionising radiation over a short period of time (low $t_{\frac{1}{2}}$)

→ LLW: e.g protective clothing, gloves, towels, implements contaminated with radiation

→ LLW stored in sealed containers [Radiation emission ends in a few days], then disposed off in landfills or sea

→ ^{99}Tc is LLW, short half life

→ HLW stored underwater in reinforced cooling ponds for 5-10 years or vitrified

→ Then, it is transfered to heavily shielded underground storage, e.g concrete bunkers, prevent contamination of water bodies

→ Innovation

- ○ extracting uranium from ash using supercritical $CO_2(l)$
- ○ replacing radionuclides with fluorescent dyes (w.r.t diagnostic medicine)

{Solvent waste}

→ synthesis and extraction of drugs involve the use of solvents

→ Why is it dangrous?

① incineration may release toxins into the environment (environmental impact) → deplete O_3 layer or add to enhanced GE

② contaminate soil/water

③ Toxic to workers (e.g carcinogenic)

④ Safety w.r.t use (flammable, explosive)

→ chlorinated compounds should be avoided → must be incinerated at high Ts to prevent the formation of carcinogenic dioxins

→ ditto for aromatic compounds

→ H_2O and supercritical $CO_2(l)$ best solvents (least harm to environment)

→ We want to limit environmental waste and reduce the use of auxillaries.

→ Recycle non-chlorinated solvents

Note: GE: greenhouse effect

Antibiotic Waste

→ extensive use of antibiotics (broad-spectrum) enables bacteria to develop resistance
→ e.g MRSA (variant of tuberculosis bacteria)
→ ↑ exposure, ↑ P(resistance developing)
→ Disposal of unused antibiotics
○ Used as prophylactic for animal lifestock → excreted into water bodies/remains in tissues → enters food chain, increasing exposure of bacteria to the antibiotics
○ Sanitizers increase exposure of bacteria to antibiotics
○ Expired unused antibiotics are discarded → contaminate water, soil → increase exposure [when you don't complete a course of antibiotics]
○ urine of people on Antibiotics → discharged into rivers → ↑ exposure
→ What ways are there to handle it?
○ minimise release into environment (destruction)
○ Complete prescribed dose
○ Do not overuse

Green Chemistry

Principles

1) High Atom Economy, Low Environmental Impact
○ Atom Economy = $\frac{M_r \text{ of desired products}}{M_r \text{ of all products}}$
○ ↑ sustainability, reduce production of unwanted products
2) Minimise steps in synthesis
○ ↑ separate steps, ↓ % yield, ↑ waste products + E used
3) Greener reactants + Solvents
○ catalysts, lower operating Ts

Case Study: Oseltamivir

- precursor for synthesis is shikimic acid or shikimate [c. base]
- found in low [ ]s in many plants, e.g Chinese star anise [used as food source as well]
- Extracted in lengthy process - low yield, used LiN_3 (unsafe)
- New Methods - ①: fermentation of genetically modified bacteria to produce shikimate
  ②: Harvesting from pine trees, more abundant resource
  ③: Extract from suspension cultures of Indian sweetgum trees

$\boxed{D7}$: Taxol

~~How is it obtained?~~

What is Taxol?

- → anti cancer drug (chemotherapeutic agent)
- → binds to tubulin, a key part of microtubules
- → Stop the breakdown of mitotic spindles in telophase, halting division
- → has 11 chiral centres, hence 22 possible enantiomers - only 1 works as a chemotherapeutic drug

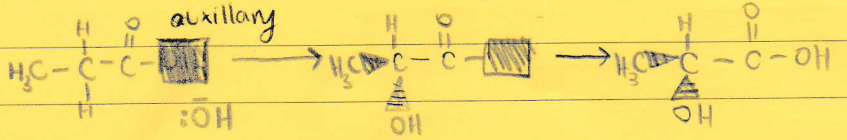
Synthesis

① Obtaining lead compounds

- → pure form could be obtained from yew trees (bark) but only 0.004% is taxol
- → stripping the bark kills the tree → not environmentally friendly
- → now, lead compound taken from leaves of yew ~~or pine~~ trees → more sustainable, no damage to plant
- → This is therefore semi-synthetic synthesis (as we use a naturally occuring lead compound to prod Taxol)
- → synthetic route - 30 steps + inefficient

② Synthesis using lead compounds

- → We use asymmetric synthesis / enantioselective synthesis
- → cannot produce racemates; enantiomers may have harmful physiological effects
- → waste of money to extract single enantiomer from a racemate → low yield [by in-vitro]
- → We utilise a chiral auxillary: an optically active substance that is temporarily incorporated into organic synthesis so it can be carried out asymmetrically.
- → binds to a site on a molecule and blocks it by steric hinderence, so the reaction can only occur with one side (forced to use a single enantiomer) (stereospecific)
- → once the enantiomer has been produced, the auxillary is recycled and reused
- → E.g synthesis of lactic acid (2-hydroxy-propanoic acid)



- → conversion of leaf compound [D10-DAB] to taxol takes 13 solvents + lots of organic reagents
- → Fungi produce taxol in fermentation reactions
- → New plant fermentation technology: extracted from plant cell cultures and extracted by chromatography → Green Chemistry (no solvents, harmful ones anyway)

Revisit the use of polarimeters!

D8: Nuclear Medicine

Date No.

Ionisation ~~Power~~ Density = $\alpha > \beta > \gamma$

Penetrating Power = $\gamma > \beta > \alpha$

Radiation

① α radiation

→ ejection of ${}^{4}_{2}\alpha$ from unstable nuclei

→ written as ${}^{4}_{2}He$ or ${}^{4}_{2}\alpha$.

→ decrease in mass by 4, decrease in proton number by 2

Example

$${}^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}\alpha$$

② Beta Radiation (β)

→ conversion of a neutron to proton and subsequent ejection of an electron and neutrino

→ no change in mass number, ↑ proton number by 1

→ written as ${}^{0}_{-1}\beta$.

Example

$${}^{234}_{90}Th \rightarrow {}^{234}_{91}Pa + {}^{0}_{-1}\beta$$

③ Gamma (γ) Radiation

→ emission of energy as photons

→ short wavelengths

→ usually accompanies α or β decay [Lutetium-177]

→ when particles and antiparticles meet

→ no change in mass or atomic number

Ionisation

→ radiation provides energy for the removal of electrons

→ lead to formation of unstable ~~radicles~~ radicals which may react immediately via oxidation reactions

→ e.g H° or OH°, acts on DNA to initiate apoptosis.

→ Ionisation Density → energy released along a unit length, highest for α due to +2 charge, then β as −1

→ Higher ID, energy release more localised, for instance, a small region in a cell

Half Lives

→ follow a first order rate reaction

Rate = $k[N]$ but as it decays with a half life = $N_T \equiv N_0 e^{-\lambda t}$ where N_T is amount at time t,

↓ ln of both sides

N_0 is initial

λ is the decay constant

PROOF ⟹

$$\ln(N_T) = \ln(N_0) - \lambda t$$

$$\ln\left(\frac{N_T}{N_0}\right) = -\lambda t$$

→ To find the decay constant / half life, we use the following derivation

let $N_T = \frac{1}{2}N_0$

NOTE that λ is in $(\text{unit time})^{-1}$

$$\ln\left(\tfrac{1}{2}\right) = -\lambda t_{\frac{1}{2}}$$

$$\ln(2) = \lambda t_{\frac{1}{2}} \quad \therefore \quad \lambda = \frac{\ln(2)}{t_{\frac{1}{2}}} \text{ and } t_{\frac{1}{2}} = \frac{\ln(2)}{\lambda}$$

FALCON

→ we can find the amount of substance remaining after t units time by this formula

$$N_T = N_0 \boxed{\left(\tfrac{1}{2}\right)^{\frac{t}{t_{\frac{1}{2}}}}} \leftarrow \text{incidentally, this is the percentage remaining}$$

e.g Find the amount of ${}^{99}_{43}Tc$ left after 8 hours if it had an initial mass of 5.00g and has a half life of 6.01 hours.

Context: ${}^{99}_{43}Tc \longrightarrow {}^{99}_{43}Tc + \gamma$

Applying

$$N_T = (N_0)\left(\tfrac{1}{2}\right)^{\frac{t}{t_{\frac{1}{2}}}} \rightarrow (5.00)\left(\tfrac{1}{2}\right)^{\frac{8}{6.01}} = \underline{\underline{1.99g}}\ (3.s.f)$$

Diagnostic Medicine

Technetium-99m (${}^{99}_{43}Te$)

- metastable radioactive isotope used in tracing (radiopharmaceutical) + artificial
- Half life of 6 hours and biological half life of 24 hours → long enough for gamma camera to detect, leaves fast enough to prevent/minimise side effects.
- generated in hospitals by decay of molybdenum-99 (β)
- releases gamma rays, penetrating (easy to detect), low ionisation (∴ low damage)
- can bind to biological molecules : allows activity of specific organs/organ systems to be studied

Iodine-131 (${}^{131}I$)

- beta + gamma emitter
- 8 hour half life + taken up by thyroid gland as thyroxin produced has 4 I atoms
- mostly used to kill thyroid tissue

Positron Emission Tomography (PET)

- administered ~~as~~ radionuclide emits positrons
- accumulates in target tissue, in which emitted positrons combine with electrons, releasing γ rays
- gamma camera allows determination of origin
- e.g ~~Flourin~~ Fluorine-18, ~~taken up~~ bonded to glucose in administered radionuclide, taken up more rapidly by cancer cells → visible on scan
- combined with computerised tomography (CT) to create PET CT to increase range of possible ~~dig~~ diagnosis.

Magnetic Resonance Imaging (MRI)

- applies HNMR
- uses shift in proton spin, uses radiowaves to induce antiparallel shift
- Computer can used to create 2 or 3-D images.
- Very useful as H atoms in water → 70% of body by mass

Radionuclide Therapy

→ the rapid division of cancer cells increase their susceptability to ionising radiation, as DNA that codes
→ for replication and mitosis are primarily affected
→ Can be external (teletherapy) or internal

External Radiotherapy

- Primarily gamma rays, directed from an external source
- $^{60}_{27}Co \longrightarrow ^{60}_{28}Ni + ^{0}_{-1}\beta + \gamma$
- Linear Accelerator: Microwave technology accelerate e^-, which are aimed at heavy metals, in order to produce high energy X-rays
- Gamma Knife Radio surgery: 200 different Co-60s produce γ rays, which converge to produce a high dose

Internal Radiotherapy

- radionuclide enters body → solid ~~or~~ (implant) or liquid
- implant can be introduced → patient needs to be isolated → radiation may have adverse effects on others

Targeted Alpha Therapy (TAT)

- can treat metastasis: inhibits production of secondary tumours
- α emitting ~~nucleotides~~ radionuclides attached to antibodies which bind to cancer antigens → specific targets.
- $^{4}_{2}\alpha$s have high ionisation density, high energy dispersed over small area - limit effect on non-target cells while killing target cells
- uses Pb-212 → alpha decay

Boron Neutron Capture Therapy

- high dose of ~~normal~~ B-10 (non radioactive) administered, collected mainly by cancer cells (R of Mitosis ↑)
- Irradiated with neutrons to produce unstable B-11. Occurs in cell, high ionisation density
- Higher p of being taken up by cancer cells, limit effects on somatic, healthy cells
- $^{10}_{5}B + ^{1}_{0}n \rightarrow ^{11}_{5}B \longrightarrow ^{4}_{2}\alpha + ^{7}_{3}Li$
- Whoever came up with this is a genius.

Side Effects of Radiotherapy

Date No.

1) Hair loss → acts on rapidly dividing follicle cells
2) Fatigue
3) Nausea
4) Sterility
5) Damage to DNA / growing / regenerating tissue

Yttrium-90 and Lutetium-177

- Yt-90 is a β emitter, but Lu-177 is β and γ
- Lu-177 has shorter penetration : ideal for smaller tumours + limit exposure of healthy cells
- Lu-177 can bind to the carrier DOTA-TATE, which attaches to specific tumours such as neuroendocrine tumours and certain thyroid cancers.

D9: Drug Detection and Analysis

Date / No.

Isolation and Purification

RECAP: Solubility

- ↑ solubility if favourable interactions can form between solute + solvent
- For n.p solvents, n.p solutes can dissolve, as LDFs can form
- For p. solvents, p. solutes can dissolve, hydrogen bonds form (or dipole dipole interactions)

Isolation (by solubility)

→ can be done by solubility differences

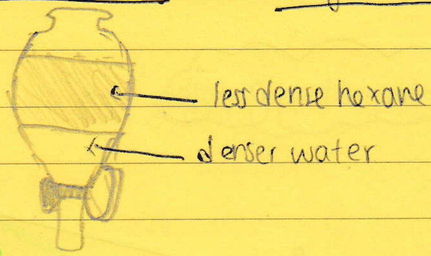
→ e.g choosing a solvent that selectively dissolves one substance over another

→ coffee beans being decaffeinated by extracting caffeine with $CO_2(l)$ is a good example

→ Solvent extraction: when one solute shows a significant difference in solubility between 2 immiscible solvents.

→ Leads to unequal distribution

→ We use a separating funnel (see RHS)



→ ① Add a solvent that a known solute A dissolves in to a ~~known~~ ageous solution of A in a separating funnel

② Shake vigorously and let it settle to allow immiscible layers to form

③ A dissolves more in the new solvent (e.g hexane) than water

④ The lower layer can therefore be drained away; it has little of solute A

⑤ Recover A by evaporation / crystallisation.

→ Depends on relative solubilities in 2 immiscible solvents

Isolation and Purification (by volatility)

RECAP: M.P + B.P

- ↑m.p, b.p with H.b > p.d - p.d > p.d - induced d > LDFs
- ↑m.p/b.p with Mr for LDFs

Fractional Distillation

→ exploits difference in volatilities

→ uses a fractionating column with glass beads to facilitate condensation, produces fractions of liquids which boil within a small range of Ts

→ isolate drug products from liquid mixtures

→ used to separate chemical feedstock

Raoult's Law

χ_A (mole fraction/chi) = $\frac{n(A)}{n(A)+n(B)}$ for a mixture of A and B

Qualitative: number of moles of A divided by the total number of moles of A and B.

Context

$$\text{liquid} \underset{\text{condense}}{\overset{\text{evap/boil}}{\rightleftharpoons}} \text{gas}$$

→ If equilibrium lies to RHS, then higher vapour pressure, more gas molecules exerting a force on liquid surface!

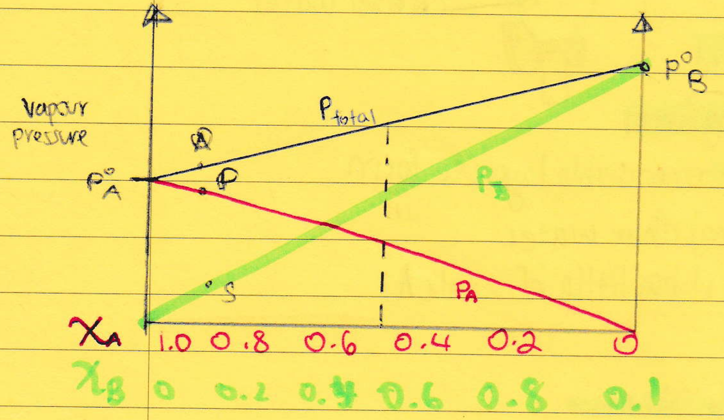
→ ∴ if we have a more volatile substance, ↑ vapour pressure

→ Total vapour pressure (P) = vapour pressure of A (P_A) + vapour pressure of B (P_B)

→ $P_A = P^o_A \cdot \chi_A$, where P^o_A is the vapour pressure of the pure substance

→ Assumptions: fully miscible substances (ideal solution) ergo form similar intermolecular forces.

Interpreting graphs



$\boxed{Q = P + S}$

○ At 0.5 each (for χ), $P_B > P_A$, ∴ higher P^o_B + ↑ proportion of B relative to A

Purification

→ we can also carry out purification with fractional distillation

→ e.g for a mixtures with $P_B > P_A$, the vapour initiatially produced by boiling a 0.6 : 0.4 ratio of A to B is enriched with B (more volatile), leading to a shift in χ_A and χ_B

→ Can repeat over several cycles

→ vapour rises up column, condenses and falls back down, reboiled by rising vapour

→ ∴ end ~~liquid~~ vapour condensed to form enriched solution with high [volatile substance]

Drug Detection

Date No.

Context

- → need methods to check on presence and [drugs] in body
- → must adhere to legal limits

Steroid Detection

- → has 4 fused rings → steroidal backbone
- → e.g male hormones (androgens)
- → anabolic steroids promote tissue growth
- → synthesised from testosterone, e.g nandrolone
- → ↑ strength + endurance but toxic to the liver + can cause cancer
- → disturb hormone balance, affect secondary sexual characteristics (hair placement + fertility)
- → we can analyse urine samples for metabolites/drugs by gas chromatography – mass spectrometry

GC-MS

- → ~~As an~~ Stationary phase: liquid coated onto a solid support (long capillary tube)
- → Mobile Phase: inert gas such as $He(g)$ or $N_2(g)$
- → separation of components in a mixture is reliant on their rates of movement
- → More volatile + less soluble, ↑ rate, vice versa
- → injected in first and boiled
- → mixes with inert gas and passes into column; some may dissolve into solvent (s. phase)
- → Each component is eluted (exits from column into detector) at different time intervals (retention time)
- → Passage of each compound represented as a peak → ergo $\int$peak = ~~tot~~ concentration relative to a standard
- → The eluted sample is then passed to a mass spec (no need to purely use retention times)
- → vapourised, ionised, passed into magnetic field, deflected + accelerated
- → RECALL* = put a +ve charge on fragment → $[C_3H_8O]^+$

Ethanol

- → polar, H-bonds with water, passes from gut via blood to several body parts
- → Hence, effects very quickly manifest in drunks.
- → Depressants: inhibit neuron transmission in the CNS, s.t changes in behaviour, possible dependency
- → judgement can become impaired.

Testing for Ethanol

Date No.

NOTE: $\underset{\text{blood}}{C_2H_5OH(aq)} \rightleftharpoons \underset{\text{exhaled breath}}{C_2H_5OH(l)}$

1. Basic Breathalyser

- use redox reaction to measure $[C_2H_5OH]$ and determine $[C_2H_5OH]_{blood}$
- $C_2H_5OH(aq) + [O] \rightarrow$ ~~C₂H~~ $CH_3COOH + H_2O$
- $Cr_2O_7^{2-}(aq)$ ~~re~~ reduced from [+6] to [+3] in $Cr^{3+}(aq)$.
- Orange → Green [crystal colour change]
- Photocell determines extent of colour change
- Finds $[C_2H_5OH]_{exhaled}$, uses K_c to find $[C_2H_5OH]_{blood}$

2. Intoximeters

- has a porous disk with Pt(s) electrodes, both saturated with acidic electrolyte
- C_2H_5OH from breath is oxidised @ anode - $C_2H_5OH(aq) + H_2O(l) \longrightarrow CH_3COOH(aq) + e^- + H_2$ $4H$
- e^- released flow from anode to cathode and H^+ used to reduce $O_2(g)$ to $H_2O(l)$
- $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
- Movement of e^- through electrical external circuit + movement of ions in electrolyte generate a current
- I used to calculate $[C_2H_5OH]_{blood}$